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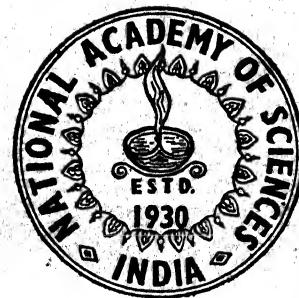
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SECTION—A

PART I

39



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Vo. XXXIX

SECTION—A

PART I

**The Fatty Acid Composition of *Sterospermum suaveolens*
Root Fat**

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[Received on 29th April, 1968]

Summary

The root fat of *Sterospermum suaveolens*^{1,2} contains palmitic, stearic and oleic acids in the following percentages 30·41, 58·16 and 11·43 respectively. A white deposit identified as ceryl alcohol has also been obtained. No unsaponifiable matter has been found in the fat indicating that all the fatty acids are present in the form of glycerides only.

Examination of the deposit from the concentrated petroleum ether solution of the root fat

The fat from the root of *Sterospermum suaveolens* was extracted with petroleum ether (40–60°) and when its concentrated solution was allowed to stand overnight, a yellowish white deposit was obtained which after purification by column chromatography over alumina and subsequent crystallisation from the hot benzene gave a pure compound melting at 79°C. Elemental analysis of the compound gave the following results. Found (C = 81·34, H = 13·98%, Molecular Weight = 309), C₂₆H₅₄O requires (C = 81·67, H = 14·13%, Molecular weight = 312). The acetyl group determination in its acetate, C₂₈H₅₆O₂, m.p. 67°C, indicated the presence of one hydroxyl group in the compound.

The compound was identified as ceryl alcohol by mixed m.p. and infrared spectrum³. Peaks in the I. R. spectrum were obtained at 3498, 2885, 2800, 1730, 1470 and 730 cm⁻¹.

Examination of fatty acids

On distilling off the solvent from the petroleum ether extract, a dark brown coloured fat (S. V. = 198·5, I. V. = 10·75) was obtained. It was saponified with 0·5 N ethanolic KOH solution and the mixed fatty acids were recovered by the usual method. The methyl esters of these acids were distilled under reduced pressure when four different fractions were obtained. The composition of each fraction was calculated with the help of their weights, saponification and iodine values and the observations and results are reported in table 1.

TABLE I

Fraction	Weight	Temp. °C	S. V.	S. E.	I. V.	Palmitic	Stearic	Oleic
1.	5.48 gm	145-50	197.91	283.33	7.70	2.18	2.80	0.50
2.	1.88 gm	150-55	195.64	286.70	6.84	0.63	1.10	0.15
3.	1.49 gm	155-60	196.15	285.70	3.57	0.47	0.90	0.12
4.	2.30 gm	Above 170	194.50	288.40	17.10	0.39	1.45	0.46
11.15			Total			3.67	6.25	1.23
			% esters			33.18	56.55	10.27
			% acids			30.41	58.16	11.43

S.V. = Saponification value

S.E. = Saponification equivalent

I.V. = Iodine value

References

- Chopra, R. N., Nayar, S. L. and Chopra, I. C., "Glossary of Indian Medicinal Plants." *C. S. I. R. Publication*, page 234.
- Kirtikar, K. R. and Basu, B. D. "Indian Medicinal Plants" Vol. III, page 1848-49.
- Bellamy, L. J. "The Infra-Red Spectra of Complex Molecules." *Methuen, London, 2nd Edition*, 1958.

Infinite integrals involving Fox's H-function and Confluent Hypergeometric Functions*

By

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[Received on 1st March, 1967]

Abstract

The object of the present paper is to evaluate some infinite integrals involving Fox's H-function and Confluent Hypergeometric functions Ξ_1 , Ξ_2 , ψ_1 , ϕ_1 and ϕ_2 by utilising a theorem recently proved by author in these proceedings. The argument of these function contain $\left(\frac{a+bt+ct^2}{t}\right)$ where 't' is the variable of integration.

1. The well known notation $L\{f(t); p\} = \phi(p)$ will be used to denote the Laplace transform,

$$(1.1) \quad \phi(p) = p \int_0^\infty e^{-pt} f(t) dt,$$

provided that the integral is convergent and $R(p) > 0$.

Recently the author [6, p. 195] has proved that, if

$$L\{f(t); p\} = g(p)$$

and

$$L\{t^{-1}f(t); p\} = h(p)$$

then

$$(1.2) \quad \int_0^\infty t^k (a + bt + ct^2)^{-1} g\left(\frac{a+bt+ct^2}{t}\right) dt = \sqrt{\frac{\pi}{c}} (b + 2\sqrt{ac})^{-1} h(b + 2\sqrt{ac}).$$

The theorem is valid for the set of conditions given below,

(A) $R(a) \geq 0$, $(c) > 0$.

(B) $R(\xi + \frac{1}{2}) > 0$, where $f(t) = 0$ (t^ξ) for small 't'.

(C) If

(i) $r < 1$; then $R(b + 2\sqrt{ac}) > 0$,

(ii) $r = 1$; then $R(\beta) < 0$, when $R(b + 2\sqrt{ac}) > R(\beta)$
and $R(\eta + \frac{1}{2}) < 0$ when $R(b + 2\sqrt{ac}) = R(\beta)$,

(iii) $r > 1$; then $R(\beta) < 0$,

where $f(t) = 0$ ($t^\eta e^{\beta t r}$) for large 't'.

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The aim of the present paper is to evaluate some infinite integrals involving Fox's H-function [4, p. 408] and confluent hypergeometric functions Π_1 , Π_2 , ψ_1 , Φ_1 and Φ_2 [3, p. 444-45].

2. In this section we shall evaluate an infinite integral involving Fox's H-function [4, p. 408]. Asymtotic expansion and analytic continuation of the H-function have been discussed by Braaksma [1].

If we start with

$$f(t) = t^\rho H_{l, q}^{m, n} \left[zt^r \middle| \begin{matrix} (a_1, e_1), \dots, (a_l, e_l) \\ (b_1, f_1), \dots, (b_q, f_q) \end{matrix} \right]$$

then [5, p. 100(8)]

$$g(p) = p^\rho H_{l+1, q}^{m, n+1} \left[zp^{-\sigma} \middle| \begin{matrix} (-\rho, \sigma), (a_1, e_1), \dots, (a_l, e_l) \\ (b_1, f_1), \dots, (b_q, f_q) \end{matrix} \right]$$

for $\sigma > 0$, $R(p) > 0$, $0 \leq m \leq q$, $0 \leq n < l$, $|\arg z| < \frac{1}{2}\lambda\pi$

where λ stands for $\sum_{j=1}^n (e_j) - \sum_{j=n+1}^l (e_j) + \sum_{j=1}^m (f_j) - \sum_{j=m+1}^q (f_j)$

and

$$R\left(\rho + 1 + \sigma \min \frac{b_h}{f_h}\right) > 0, \quad h = 1, \dots, m.$$

Similarly the expression for $h(p)$ can be obtained and hence applying (1.2), we obtain

$$(2.1) \quad \int_0^\infty t^{\rho+\frac{1}{2}} (a + bt + ct^2)^{-\rho-1} H_{l+1, q}^{m, n+1} \left[\begin{matrix} zt^r \\ (a + bt + ct^2)^r \end{matrix} \middle| \begin{matrix} (-\rho, \sigma), (a_1, e_1), \\ \dots, (a_l, e_l) \\ \dots, (b_q, f_q) \end{matrix} \right] dt \\ = \sqrt{\frac{\pi}{c}} (b + 2\sqrt{ac})^{-\rho-\frac{1}{2}} H_{l+1, q}^{m, n+1} \left[\begin{matrix} z \\ b + 2\sqrt{ac} \end{matrix} \middle| \begin{matrix} (\frac{1}{2} - \rho, \sigma), (a_1, e_1), \\ \dots, (a_l, e_l) \\ \dots, (b_q, f_q) \end{matrix} \right]$$

valid for $\sigma > 0$, $R(a) > 0$, $c > 0$, $R(b + 2\sqrt{ac}) > 0$, $0 \leq m \leq q$,

$0 \leq n \leq l$, $R\left(\rho - \frac{1}{2} + \sigma \min \frac{b_h}{f_h}\right) > 0$, $h = 1, \dots, m$, $\lambda > 0$ and
 $|\arg z| < \frac{1}{2}\lambda\pi$

where λ stands for $\sigma + \sum_{j=1}^n (e_j) - \sum_{j=n+1}^l (e_j) + \sum_{j=1}^m (f_j) - \sum_{j=m+1}^q (f_j)$.

When $\sigma = e_1 = \dots = e_q = f_1 \dots = f_q = 1$ then (2.1) reduces to a known result due to Saxena [7, p. 663(5)].

3. In this section we shall evaluate certain infinite integrals involving confluent hypergeometric functions Π_1 , Π_2 , ψ_1 , Φ_1 , and Φ_2 [3, p. 444–45].

If we take

$$f(t) = t^{\alpha'-1} \Pi_2(\alpha, \beta, \gamma; x, yt)$$

then [2, p. 223(15)]

$$g(p) = \Gamma(\alpha') p^{1-\alpha'} \Pi_1\left(\alpha, \alpha', \beta, \gamma; x, \frac{y}{p}\right)$$

for $R(\alpha') > 0$, $R(p) > 0$, $R(y)$.

Similarly the expression for $h(p)$ can be obtained and hence using (2.1), we get

$$(3.1) \quad \int_0^\infty t^{\alpha'-1} (a + bt + ct^2)^{-\alpha'} \Pi_1\left(\alpha, \alpha', \beta, \gamma; x, \frac{yt}{a + bt + ct^2}\right) dt \\ = \sqrt{\frac{\pi}{c}} (b + 2\sqrt{ac})^{\frac{1}{2}-\alpha'} \Gamma(\alpha' - \frac{1}{2}) \{ \Gamma(\alpha') \}^{-1} \Pi_1\left(\alpha, \alpha' - \frac{1}{2}, \beta, \gamma; x, \frac{y}{b + 2\sqrt{ac}}\right)$$

for $R(a) > 0$, $c > 0$, $R(\alpha' - \frac{1}{2}) > 0$ and $R(b + 2\sqrt{ac}) > 0$.

When $b = c = 1$, a and x tends to zero than (3.1) reduces to the particular case of a known result [3, p. 417(21)].

Results (3.2), (3.3), (3.4) and (3.5) can similarly be obtained by using the operational pairs [2, p. 222–23. (6), (12), (10) and (7)], respectively.

$$(3.2) \quad \int_0^\infty t^{\alpha-\frac{1}{2}} (a + bt + ct^2)^{-\alpha} \Pi_2\left(\alpha, \beta, \gamma; \frac{xt}{a + bt + ct^2}, y\right) dt \\ = \sqrt{\frac{\pi}{c}} \frac{\Gamma(\alpha - \frac{1}{2})}{\Gamma(\alpha)} (b + 2\sqrt{ac})^{\frac{1}{2}-\alpha} \Pi_2\left(\alpha - \frac{1}{2}, \beta, \gamma; \frac{x}{b + \sqrt{ac}}, y\right),$$

for $R(a) > 0$, $c > 0$, $R(\alpha - \frac{1}{2}) > 0$, and $R(b + 2\sqrt{ac}) > 0$.

$$(3.3) \quad \int_0^\infty t^{\beta-1} (a + bt + ct^2)^{-\beta} \psi_1\left(\alpha, \beta, \gamma, \gamma'; \frac{xt}{a + bt + ct^2}, y\right) dt \\ = \sqrt{\frac{\pi}{c}} \frac{\Gamma(\beta - \frac{1}{2})}{\Gamma(\beta)} (b + 2\sqrt{ac})^{\frac{1}{2}-\beta} \psi_1\left(\alpha, \beta - \frac{1}{2}, \gamma, \gamma'; \frac{x}{b + 2\sqrt{ac}}, y\right),$$

for $R(a) \geq 0$, $c > 0$, $R(\beta - \frac{1}{2}) > 0$ and $R(b + 2\sqrt{ac}) > 0$.

$$(3.4) \quad \int_0^\infty t^{\alpha-\frac{1}{2}} (a + bt + ct^2)^{-\alpha} \Phi_1\left(\alpha, \beta, \gamma; \frac{xt}{a + bt + ct^2}, \frac{yt}{a + bt + ct^2}\right) dt \\ = \sqrt{\frac{\pi}{c}} \frac{\Gamma(\alpha - \frac{1}{2})}{\Gamma(\alpha)} (b + 2\sqrt{ac})^{\frac{1}{2}-\alpha} \Phi_1\left(\alpha - \frac{1}{2}, \beta, \gamma; \frac{x}{b + 2\sqrt{ac}}, \frac{y}{b + 2\sqrt{ac}}\right),$$

for $R(a) \geq 0$, $c > 0$, $R(a - \frac{1}{2}) > 0$, and $R(b + 2\sqrt{ac}) > 0$.

$$(3.5) \quad \int_0^\infty t^{\beta'-1} (a + bt + ct^2)^{-\beta'} \Phi_2 \left(\beta, \beta', \gamma; x, \frac{yt}{a + bt + ct^2} \right) dt \\ = \sqrt{\frac{\pi}{c}} \frac{\Gamma(\beta' - \frac{1}{2})}{\Gamma(\beta')} (b + 2\sqrt{ac})^{1-\beta'} \Phi_2 \left(\beta, \beta' - \frac{1}{2}, \gamma; x, b + \frac{y}{2\sqrt{ac}} \right),$$

for $R(a) \geq 0$, $c > 0$, $R(\beta' - \frac{1}{2}) > 0$, and $R(b + 2\sqrt{ac}) > 0$.

The author is grateful to Dr. P. N. Rathie for his keen interest during the preparation of this paper.

References

1. Braaksma, B. L. J. Asymptotic expansions and analytic continuations for a class of Barnes's integrals. *Composito Math.*, **15**: 239-341, 1963.
2. Erdelyi, A. et al. Tables of integral transforms, Vol. I : McGraw-Hill, New York, 1954.
3. Erdelyi, A. et al. Tables of integral transforms, Vol. II : McGraw-Hill, New York, 1954.
4. Fox, G. The G and H-function as symmetrical Fourier kernels. *Trans. Amer. Math. Soc.*, **98** : 395-429, 1961.
5. Gupta, K. C. On the H-functions. *Annales de la Soc. Sci. de Bruxelles*, **79** : 97-106, 1965.
6. Kalla, S. L. Some infinite integrals involving generalized Hypergeometric Functions ψ_2 and F_c . *Proc. Nat. Acad. Sci. India*, **37A (ii)**, 195-200, 1967.
7. Saxena, R. K. An Integral involving G-function. *Proc. Nat. Inst. Sci. India*, **26** : 661-664, 1960.

On the Steady flow of Reiner-Philippoff fluid between Parallel plates and Coaxial cylinders in linear movement

By

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[Received on 28th January, 1967]

Summary

In the first part of the paper we have discussed the flow of Reiner-Philippoff fluid through a channel bounded by two parallel plates in linear movement. The velocity profiles have been drawn for two important non-Newtonian fluids, Molten Sulphur and 0·4% Polysterene in Tetralin. Expressions for the longitudinal velocity in the case of porous plates have also been derived. In the second part, the flow of Reiner-Philippoff fluid through an annulus, having boundaries in linear movement has been investigated and the axial velocity profiles have been drawn. The zero shear stress surfaces have also been marked. Further we note that the variations in longitudinal velocities are more marked in 0·4% Polysterene in Tetralin than Molten Sulphur as we move from one boundary to the other.

1. Introduction

The flow equations of many non-Newtonian fluids are applicable in the field of chemical and mechanical engineering. These equations have earlier been derived empirically from the test-data. A more rigorous approach to the flow problems is essential due to the increasing importance of these fluids. The flow channels composed of two parallel plates or coaxial cylindrical boundaries, in linear movement, having different constant velocities are of interest in viscosity pump and screw extruder design. Rotem and Shinner [1] have solved the flow equations of non-Newtonian inelastic fluid for the case of steady, incompressible laminar flow between parallel boundaries in linear movement with an arbitrary pressure gradient. Solution has also been given for (i) Rabinowitsch model, and (ii) Power-law pseudoplastic model. Fredrickson and Bird [2] have studied one-dimensional steady flow of Power-law pseudoplastic and Bingham Plastic fluid through an annulus. Rotem [3] has obtained the velocity profiles and flow rate for the steady, isothermal and laminar flow of an incompressible, inelastic non-Newtonian fluid in an annulus. A solution for the Rabinowitsch equation type of pseudoplastic fluid has also been obtained as a special case. Kapur and Gupta [4] have discussed the flow of Reiner-Philippoff fluid in pipes and channels. The rheological equation for this fluid is given by [5],

$$\tau_{ij} = \left[\mu_0 + \frac{\mu_\infty - \mu_0}{1 + (\tau_{lm} \tau_{lm})/2\tau_0^2} \right] \epsilon_{ij}, \quad (1.1)$$

where μ_0 , μ_∞ and τ_0 are the fluid parameters and usual summation convention has been assumed for repeated index. This model reduces to a Newtonian fluid with viscosity μ_0 or μ_∞ according as $\tau_0 \rightarrow 0$ or $\tau_0 \rightarrow \infty$. But the behaviour is non-Newtonian for every other value of τ_0 .

The present paper is divided into two parts. In part A the steady flow of Reiner-Philippoff model between parallel boundaries in linear movement with constant pressure gradient has been investigated following [1]. The physical constants of Molten Sulphur and 0·4% Polysterene in Tetralin have been taken respectively, for very small and large values of τ_0 , in order to draw the velocity profiles for two limiting cases of the fluid parameter τ_0 . The expression for the velocity distribution in the case of two porous plates in linear movement has also been obtained. In part B, the flow of the same fluid between two coaxial cylindrical boundaries in linear movement and under constant pressure gradient has been discussed. The velocity profiles in the two extreme cases for the same fluids as taken in part A, have also been plotted.

Part A : Flow between two parallel plates

2. Formulation of the problem

Let x -axis be parallel to the plates and y -axis be perpendicular to them. Let u and v be the components of velocities along x and y axes respectively. The plates are defined by the equations $y = -h$ and $y = h$, having the velocities u_1 and u_2 parallel to x -axis. For the two dimensional flow, the velocity components are

$$u = u(y), v = 0. \quad (2\cdot1)$$

Therefore the equations of motion reduce to

$$\begin{aligned} 0 &= -\partial p/\partial x + \partial \tau_{xy}/\partial y, \\ 0 &= -\partial p/\partial y, \end{aligned} \quad (2\cdot2)$$

where p is the pressure.

The non-zero components of deviatoric stress tensor are given by

$$\tau_{xy} = \left[\mu_0 + \frac{(\mu_\infty - \mu_0) \tau_0^2}{\tau_0^2 + \tau_{xy}^2} \right] e_{xy}. \quad (2\cdot3)$$

We define the following non-dimensional quantities

$$X = x/h, Y = y/h, \mu = \mu_\infty/\mu_0, U = u/u_1, U' = u_2/u_1. \quad (2\cdot4)$$

$$P = p/\rho u_1^2, T_{xy} = \tau_{xy}/\rho u_1^2, E_{xy} = \mu_0 e_{xy}/\rho u_1^2, T_0 = \tau_0/\rho u_1^2. \quad (2\cdot5)$$

Substituting equation (2·4) and (2·5) in (2·2) and (2·3) we get

$$\begin{aligned} \partial T_{xy}/\partial Y &= \partial P/\partial X, \\ \text{and } T_{xy} &= [1 + (\mu - 1) T_0^2/(T_0^2 + T_{xy}^2)] E_{xy}, \\ \text{where } E_{xy} &= \partial U/\partial Y. \end{aligned} \quad \left. \right\} \quad (2\cdot6)$$

3. Solution of the equations

We apply constant pressure gradient on the fluid. Therefore, we have

$$-\partial P/\partial X = P'. \quad (3\cdot1)$$

Equation (3·1) and first equation of (2·6) give

$$T_{xy} = P'(Y_0 - Y), \quad (3\cdot2)$$

where $Y = Y_0$ denotes the zero shear stress plane.

Substituting equation (3.2) in second equation of (2.6) we get

$$\partial U / \partial T = P' (\gamma_0 - \gamma) + [P' T_0^2 (1 - \mu) (\gamma_0 - \gamma) / \{P'^2 (\gamma_0 - \gamma)^2 + \mu T_0^2\}] \quad (3.3)$$

Integration of (3.3) gives

$$2 P' (U + 1) = P'^2 [2 \gamma_0 (\gamma + 1) - (\gamma^2 - 1)] - \\ - (B_1/2) \ln [\{P'^2 (\gamma_0 - \gamma)^2 + \mu T_0^2\} / \{P'^2 (\gamma_0 + 1)^2 + \mu T_0^2\}]$$

for $-1 \leq \gamma \leq \gamma_0$, and

(3.4)

$$2 P'^2 (U' - U) = P'^2 [2 \gamma_0 (1 - \gamma) + \gamma^2 - 1] - \\ - (B_1/2) \ln [\{P'^2 (1 - \gamma_0)^2 + \mu T_0^2\} / \{P'^2 (\gamma - \gamma_0)^2 + \mu T_0^2\}],$$

for $\gamma_0 \leq \gamma \leq 1$ and,

$$B_1 = 2 (1 - \mu) T_0^2,$$

where the lower plate is assumed to be moving in a direction opposite to that of the upper plate.

Equating the velocities obtained from both the equations (3.4) at $\gamma = \gamma_0$, we get

$$2 P' (U' + 1) = 4 P'^2 \gamma_0 - (B_1/2) I_n [\{P'^2 (n - \gamma_0)^2 + \mu T_0^2\} \times \\ \times \{P'^2 (1 + \gamma_0)^2 + \mu T_0^2\}^{-1}] \quad (3.5)$$

From the above equation we infer that the constant γ_0 cannot be determined explicitly. Hence we consider two limiting cases i.e. T_0 is very small and T_0 is very large.

When T_0 is small we assume

$$\gamma_0 = \gamma_1 + \gamma_2 T_0^2. \quad (3.6)$$

On neglecting second and higher powers of T_0^2 the equations (3.5) and (3.6) give

$$\gamma_1 = (U' + 1) / 2P',$$

and $\gamma_2 = \{(1 - \mu) / 2P'^2\} \ln [(2P' - U' - 1) / (2P' + U' + 1)]$, (3.7)

where values of U' and P' should satisfy

$$|(U' + 1) / 2P'| < 1,$$

so that the zero shear surface may lie within the boundaries.

When T_0 is large we assume

$$\gamma_0 = \gamma_1' + \gamma_2' / T_0^2. \quad (3.8)$$

Substituting (3.8) in (3.5) and neglecting second and higher powers of $(1/T_0^2)$, we get

$$\gamma_1' = \mu (U' + 1) / 2P',$$

and $\gamma_2' = (1 - \mu) P' \gamma_1' (1 + \gamma_1'^2) / \mu$, (3.9)

where values of U' and P' should satisfy

$$|\mu (U' + 1) / 2P'| < 1,$$

so that the zero shear stress surface may lie within the boundaries.

4. Numerical calculation

In literature [5] we find Molten Sulphur and 0·4% Polyesterene in Tetralin as two important Reiner-Philippoff fluids having the small and large values of τ_0 respectively. The fluid parameters for these fluids are,

(i) Molten Sulphur

$$\mu_\infty = 0\cdot215 \text{ poises}, \mu_0 = 0\cdot0105 \text{ poises}, \tau_0 = 0\cdot073 \text{ dynes/cm}^2 \quad (4\cdot1)$$

(ii) 0·4% Polyesterene in Tetralin

$$\mu_\infty = 4\cdot0 \text{ poises}, \mu_0 = 1\cdot0 \text{ poise}, \tau_0 = 500 \text{ dynes/cm}^2. \quad (4\cdot2)$$

Longitudinal velocity profiles for these two fluids, have been plotted against Y in figure 1. The zero shear stress planes are marked in various curves.

We infer from figure 1, that for Molten Sulphur as well as 0·4% Polyesterene in Tetralin, the zero shear stress planes moves towards the lower plate with the increase of pressure gradient. For the same pressure gradient the variations in magnitude of longitudinal velocity are more marked in Molten Sulphur than 0·4% Polyesterene in Tetralin.

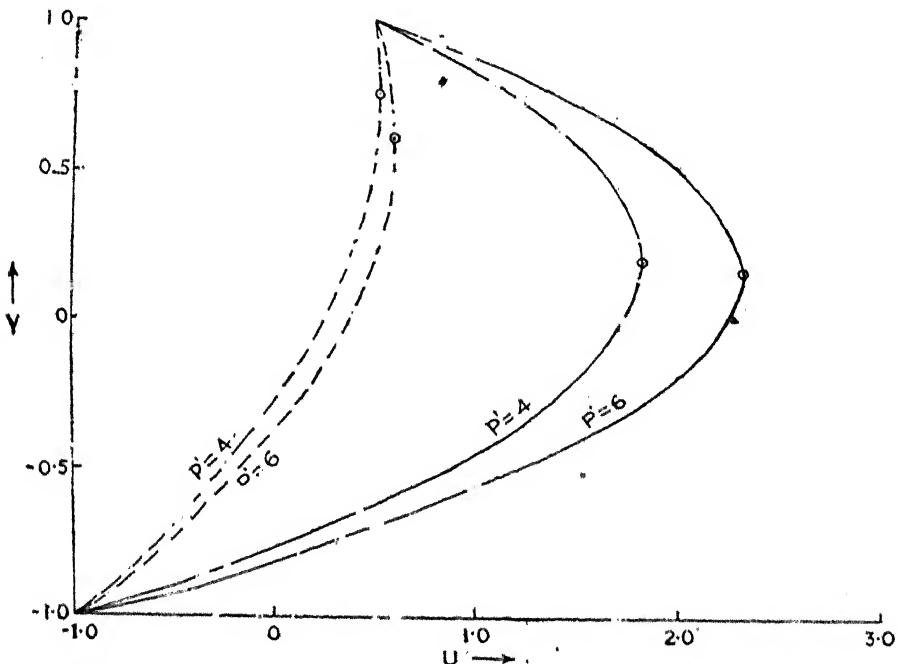


Fig.1 LONGITUDINAL VELOCITY PROFILES AGAINST Y
 — Molten Sulphur, - - - 0·4% Polyesterene in Tetralin.
 ○ Position of zero shear stress plane

5. Flow between two porous plates

Let the orientation and the velocities of the plates be the same as in section 2. We assume the rate of suction v_0 at the upper plate is equal to the rate of injection at the lower plate. From the equation of continuity we find

$$u = u(y), v = v_0. \quad (5\cdot1)$$

The equations of motion, therefore, reduce to

$$\left. \begin{aligned} \rho v_0 \frac{\partial u}{\partial y} &= -\frac{\partial p}{\partial x} + \frac{\partial \tau_{xy}}{\partial y}, \\ 0 &= -\frac{\partial p}{\partial y} \end{aligned} \right\} \quad (5.2)$$

where ρ is the density and p is pressure.

The non-zero component of deviatoric stress tensor is given by (2.3). In addition to the non-dimensional quantities defined in (2.4) we define the following quantities :

$$\begin{aligned} P &= 2 h p / \mu_0 u_1, \quad T_0 = 2 h \tau_0 / \mu_0 u_1, \quad T_{xy} = 2 h \tau_{xy} / \mu_0 u_1, \\ E_{xy} &= 2 h e_{xy} / u_1, \quad R = 2 h v_0 \rho / \mu_0, \end{aligned} \quad (5.3)$$

where R is the suction parameter.

From equation (2.3), (2.4), (5.2) and (5.3) we have

$$\begin{aligned} \text{and } \frac{\partial T_{xy}}{\partial Y} &= -P' + R \frac{\partial U}{\partial Y}, \\ T_{xy} &= [1 + (\mu - 1) T_0^2 / (T_{xy}^2 + T_0^2)] \varepsilon_{xy}, \end{aligned} \quad (5.4)$$

where

$$-\frac{\partial P}{\partial X} = P'.$$

Integrating first equation of (5.4) and eliminating T_{xy} from second equation of (5.4) we get

$$\begin{aligned} \frac{\partial U}{\partial Y} &= (-P'Y + RU + A) [T_0^2 + (-P'Y + RU + A)^2] \times [\mu T_0^2 + \\ &\quad + (-P'Y + RU + A)^2]^{-1}, \end{aligned} \quad (5.5)$$

where A is the constant of integration. Boundary conditions of the flow are

$$\left. \begin{aligned} U &= U' \text{ at } Y = 1, \\ U &= -1 \text{ at } Y = -1. \end{aligned} \right\} \quad (5.6)$$

Solution of (5.5) is obtained for two extreme cases, T_0^2 is small or large.

Case (i) : Small T_0^2 .

We neglect second and higher degree terms in T_0^2 in (5.5). Subsequent integration gives

$$\begin{aligned} Y + 1 &= (1/R) \ln [(-RP'Y + R^2U + RU - P') / (RP' - R^2 + RA - P')] + \\ &+ (RT_0^2/P') (\mu - 1) [(RP' - R^2 + RA - P')^{-1} - (-RP'Y + R^2U + RA - P')^{-1} + \\ &+ (P')^{-1} \ln \{(-P'Y + RU + A) (RP' - R^2 + RA - P') (P - R + A)^{-1} \times \\ &\times (-RP'Y + R^2U + RA - P')^{-1}\}]. \end{aligned} \quad (5.7)$$

In order to determine A explicitly we assume

$$A = A_0 + A_1 T_0^2. \quad (5.8)$$

From equations (5.6), (5.7) and (5.8) we have

$$\begin{aligned} A_0 &= [-RP' + R^2U' - P' + (-RP' + R^2 + P') \exp(2R)] \times \\ &\times [R \{\exp(2R) - 1\}]^{-1}, \end{aligned}$$

and

$$A_1 = R(1-\mu) (P')^{-2} [P' + (-RP' + R^2U' - P' + RA_0) \times \\ \times \{ \ln(-P' + RU' + A_0) - \ln(P' - R + A_0) - 2R \} \{\exp(2R) - 1\}]^{-1}. \quad (5.9)$$

Case (ii) : Large T_0^2

We neglect second and higher degree terms in $(1/T_0^2)$ in (5.5). Subsequent integration gives

$$r + 1 = (\mu/R) \ln [(-RP'Y + R^2U + RA - \mu P') (RP' - R^2 + RA - \mu P')^{-1}] + \\ + (1-\mu) (RT_0)^{-2} [(3\mu^2 P'^2/R) \ln \{(-RP'Y + R^2U + RA - \mu P') \times \\ \times (RP' - R^2 + RA - \mu P')^{-1}\} + 0.5 (-P'Y + RU - P' + R) (-RP'Y + \\ + R^2U + RP' - R^2 + 2AR + 4\mu P') + (\mu^3 P'^3/R) \{(RP' - R^2 + \\ + RA - \mu P')^{-1} - (-RP'Y + R^2U + RA - \mu P')^{-1}\}]. \quad (5.10)$$

In order to determine A explicitly we assume

$$A = A_0 + (A_1/T_0^2). \quad (5.11)$$

From equations (5.6), (5.10) and (5.11) we have

$$A_0 = [-RP' + R^2U' - \mu P' - (RP' - R^2 - \mu P') \exp(2R/\mu)] \times \\ \times [R \{ \exp(2R/\mu) - 1 \}]^{-1},$$

and

$$A_1 = \mu^2 P'^3 (1-\mu)/R^3 + (1-\mu) (-RP' + R^2U' - \mu P' + RA_0) \times \\ \times \{6\mu P'^2 + (-2P' + RU' + R) (R^2U' - R^2 + 2RA_0 + 4\mu P')\} \times \\ \times [2\mu R^2 \{ \exp(2R/\mu) - 1 \}]^{-1}. \quad (5.12)$$

Part B : Flow between two coaxial cylinders

6. The basic equations

The fluid is contained between two infinitely long coaxial cylinders of radii a and b ($b > a$). We shall work through cylindrical polar coordinates (r, θ, z) . Let u , v , and, w be the components of the velocity in the direction of r , θ , z respectively. We assume the axial velocities of inner and outer cylinder to be w_1 and w_2 , respectively. Hence we have

$$u = 0, v = 0, w = w(r). \quad (6.1)$$

The equations of motion reduce to

$$\left. \begin{aligned} -\partial p/\partial r &= 0, \\ -\partial p/\partial z + r^{-1} \partial(r \tau_{rz})/\partial r &= 0 \end{aligned} \right\} \quad (6.2)$$

where p is the pressure

The non-zero deviatoric stress component is

$$\tau_{rz} = [\mu_0 + (\mu_\infty - \mu_0) \tau_0^{-2}/(\tau_0^{-2} + \tau_{rz}^{-2})] e_{rz} \quad (6.3)$$

Let us define the following non-dimensional quantities :

$$\begin{aligned}\zeta &= z/a, R = r/a, \alpha = b/a, W = w/w_1, W' = w_2/w_1, \mu = \mu_\infty/\mu_0, \\ P &= p/\rho w_1^2, T_{rz} = \tau_{rz}/\rho w_1^2, T_0 = \tau_0/\rho w_1^2, E_{rz} = e_{rz} \rho w_1^2/\mu_0.\end{aligned}\quad (6.4)$$

Equations (6.2), (6.3) and (6.4) give

$$\left. \begin{aligned}R^{-1} \frac{\partial(RT_{rz})}{\partial R} &= \frac{\partial P}{\partial \zeta}, \\ T_{rz} &= [1 + (\mu - 1) T_0^2 / (T_0^2 + T_{rz}^2)] E_{rz}\end{aligned}\right\} \quad (6.5)$$

where $E_{rz} = \partial W / \partial R$.

Equations (6.5) determine the motion of the fluid completely.

7. Solution of equations

Let us consider that the motion takes place under constant pressure gradient. Therefore we have

$$-\frac{\partial P}{\partial \zeta} = P'. \quad (7.1)$$

Equation (7.1) and first equation of (6.5) give

$$T_{rz} = P' (R_0^2 - R^2) / 2R, \quad (7.2)$$

where $R = R_0$ denotes zero shear stress surface. Equation (7.2) and second equation of (6.5) give

$$\frac{\partial W}{\partial R} = P' (R_0^2 - R^2) \{ \mu D (R_0^2 - R^2) + 2R^2 \} / [2 \mu R \{ D(R_0^2 - R^2) + 2R^2 \}], \quad (7.3)$$

where $D = P'/2 \mu T_0^2$.

We assume that inner cylinder is moving in a direction opposite to that of the outer cylinder. The equation (7.3) is integrated for the following two cases :

(i) where $T_0^2 < R_0^2 P'^2 / \mu$ the axial velocity is given by

$$\begin{aligned}4P' (W + 1) &= P'^2 (P_0^2 \ln R^2 - R^2 + 1) - B_2 \ln [\{D(R_0^2 - R^2)^2 + 2R^2\} \times \\ &\times \{D(R_0^2 - 1)^2 + 2\}^{-1}] + (2B_2/B_3) \tan^{-1} [B_3(R^2 - 1) \{R^2 + 1 + \\ &\times D(R_0^2 - R^2)(R_0^2 - 1)\}^{-1}],\end{aligned}\quad (7.4)$$

for $1 \leq R \leq R_0$, and

$$\begin{aligned}4P'_1 (W - W') &= P'^2 (\alpha^2 - R^2 - R_0^2 \ln \alpha^2/R^2) + B_2 \ln [\{(\alpha^2 - R^2)D + 2\alpha^2\} \times \\ &\times \{(R^2 - R_0^2)D + 2R^2\}^{-1}] - (2B_2/B_3) \tan^{-1} [B_3(\alpha^2 - R^2) \{R^2 + \alpha^2 + \\ &\times D(R^2 - R_0^2)(\alpha^2 - R_0^2)\}^{-1}],\end{aligned}\quad (7.5)$$

for $R_0 \leq R \leq \alpha$,

where $B_2 = 2(1 - \mu) T_0^2$,

and $B_3 = \sqrt[R_0^2 P'^2 / \mu T_0^2 - 1]$.

Equating the velocities at $R = R_0$, obtained from equation (7.4) and (7.5) we get

$$4P'(W' + 1) = P'^2 (R_0^2 \ln \alpha^2 - \alpha^2 + 1) - B_2 \ln [\{ D(\alpha^2 - R_0^2)^2 + 2\alpha^2 \} \times \\ \times \{ D(R_0^2 - 1)^2 + 2 \}^{-1}] + (2B_2/B_3) \tan^{-1} [B_3(\alpha^2 - 1) \{ \alpha^2 + 1 - \\ \times D(R_0^2 - 1) (\alpha^2 - R_0^2) \}^{-1}]. \quad (7.6)$$

(ii) when $T_0^2 > R_0^2 P'^2 / \mu$ the axial velocity is given by

$$4P'(W + 1) = P'^2 (R_0^2 \ln R^2 - R^2 + 1) - B_2 \ln [\{ D(R_0^2 - R^2) + 2R^2 \} \times \\ \times \{ D(R_0^2 - 1)^2 + 2 \}^{-1}] - (B_2/B_4) \ln [\{ D(R_0^2 - R^2) (R_0^2 - 1) + R^2 + 1 - \\ - B_4(R^2 - 1) \} \{ D(R_0^2 - R^2) (R_0^2 - 1) + R^2 + 1 + B_4(R^2 - 1) \}^{-1}], \quad (7.7)$$

for $1 \leq R \leq R_0$, and

$$4P'(W - W') = P'^2 (\alpha^2 - R^2 - R_0^2 \ln \alpha^2/R^2) + B_2 \ln [\{ D(\alpha^2 - R_0^2)^2 + 2\alpha^2 \} \times \\ \times \{ D(R_0^2 - R_0^2)^2 + 2R^2 \}^{-1}] - (B_2/B_4) \ln [\alpha^2 + R^2 + B_4(\alpha^2 - R^2) + D(\alpha^2 - R_0^2) \times \\ \times R^2 - R_0^2 \} \{ \alpha^2 + R^2 - B_4(\alpha^2 - R^2) \}^{-1} + D(\alpha^2 - R_0^2, (R^2 - R_0^2)^{-1}], \quad (7.8)$$

for $R_0 \leq R \leq a$,

$$\text{where } B_4 = \sqrt{1 - R_0^2 P'^2 / \mu T_0^2}.$$

Equating the value of W obtained from the equations of (7.7) and (7.8) at $R = R_0$, we get

$$4P'(W' + 1) = P'^2 (R_0^2 \ln \alpha^2 - \alpha^2 + 1) - B_2 \ln [\{ D(\alpha^2 - R_0^2)^2 + 2\alpha^2 \} \times \\ \times \{ D(R_0^2 - 1)^2 + 2 \}^{-1}] - (B_2/B_4) \ln [\{ \alpha^2 + 1 - B_4(\alpha^2 - 1) - D(R_0^2 - 1) \times \\ \times (\alpha^2 - R_0^2) \} \{ \alpha^2 + 1 - B_4(\alpha^2 - 1) - D(R_0^2 - 1) (\alpha^2 - R_0^2) \}^{-1}]. \quad (7.9)$$

From equations (7.9) and (7.6), it is clear that R_0 cannot be determined explicitly. When T_0 is small, we assume

$$R_0^2 = R_1^2 + T_0^2 R_2^2. \quad (7.10)$$

Substituting (7.10) in (7.6) and neglecting fourth and higher powers of T_0 , we get

$$R_1^2 = [P'(\alpha^2 - 1) + 4(W' + 1)]/2P' \ln a, \quad \left. \begin{array}{l} \\ \end{array} \right\}$$

and

$$R_2^2 = \left. \begin{array}{l} \{ 4(1 - \mu)/2P'^2 \ln a \} \ln [\{ P'(\alpha^2 \ln \alpha^2 - \alpha^2 + 1) - \\ - 4(W' + 1) \} \{ P'(\alpha^2 - \ln \alpha^2 - 1) + 4(W' + 1) \}^{-1}], \end{array} \right\} \quad (7.11)$$

where W' , P' , and a should satisfy the condition

$$1 < [\{ P'(\alpha^2 - 1) + 4(W' + 1) \} / 2P' \ln a] < \alpha^2,$$

so that the zero shear stress surface may lie within the boundaries.

When T_0 is large we assume

$$R_0^2 = R_3^2 + R_4^2/T_0^2. \quad (7.12)$$

Substituting equation (7.12) in equation (7.9) and neglecting fourth and higher powers of $(1/T_0)$, we get

$$\text{and } \left. \begin{aligned} R_3^2 &= [P'(\alpha^2 - 1) + 4\mu(W' + 1)]/2P' \ln \alpha, \\ R_4^2 &= \{P'(1 - \mu)/8\mu^2\alpha^2 \ln \alpha^2\} [(\alpha^2 - 1)(2R_3^6 + 6\alpha^2R_3^2 - \alpha^2 - \alpha^4) - 6R_3^4\alpha^2 \ln \alpha^2]. \end{aligned} \right\} \quad (7.13)$$

where W' , P' , and α should satisfy the condition

$$1 < [P'(\alpha^2 + 1) + 4\mu(W' + 1)]/2P' \ln \alpha < \alpha^2,$$

so that the zero shear stress surface may lie within the boundaries.

8. Numerical calculation

Axial velocity profiles for two fluids whose parameters are defined by (4.1) and (4.2) are drawn against R in figure 2. From figure 2, we infer, that for Molten Sulphur as well as 0.4% Polystyrene in Tetralin, the zero shear stress surface moves towards the inner cylinder with increase of pressure gradient.

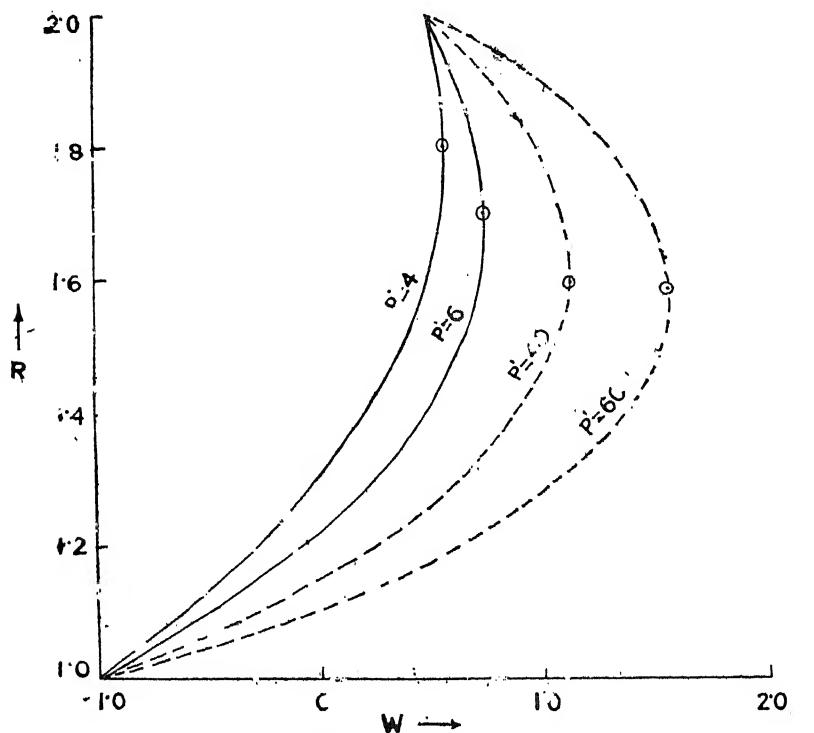


Fig 2: Axial Velocity Profile Against R
— Molten Sulphur, --- 0.4% Polystyrene in Tetralin
○ Position zero shear stress surface

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References

1. Z. Rotem and R. Shinnar, Non-Newtonian flow between parallel boundaries in linear movement. *Chemical Engineering Science*, **15** : 130, 1961.
2. R. B. Bird, W. E. Stewart, and E. N. Lightfoot. *Transport Phenomena*, John Wiley and Sons, 1961.
3. A. G. Fredrickson and R. B. Bird. Non-Newtonian flow in annuli. *Industrial and Engineering Chemistry*, **50** : 347, 1958.
4. Z. Rotem. Non-Newtonian flow in annuli. *Journal of Applied Mechanics*, **29** : 421, 1962.
5. J. N. Kapur and R. C. Gupta. Motion of Ellis and Reiner-Philippoff fluid in pipes and channels. *Archivum Mechaniki Stosowanej*, **17** : 31, 1965.

Calcium carbonate - Phosphoric acid neutralisation at 5° and 30°C

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Abstract

The electric conductivity results show that there is gradual fall in the values when calcium carbonate is added to phosphoric acid in the molecular ratio of $\text{CaCO}_3 : \text{P}_2\text{O}_5$ as 1 : 1, 2 : 1 and 3 : 1. Maximum number of ions are removed from the solution when calcium carbonate is added to phosphoric acid in the ratio of 3 : 1. The pH determinations indicate that the hydrogen ion concentration decreases with the increasing amounts of calcium carbonate added.

Dicalcium phosphate with different degrees of hydration is invariably obtained when calcium carbonate and phosphoric acid are mixed in the molecular ratio of $\text{CaCO}_3 : \text{P}_2\text{O}_5$ as 1 : 1 and 2 : 1. It has been found that with the decrease in the concentration of the acid, the solid residue has a tendency to pass from anhydrous to hydrated form. The neutralization of phosphoric acid with calcium carbonate in the ratio of $\text{CaCO}_3 : \text{P}_2\text{O}_5$ as 2 : 1 is more efficient at 5°C than at 30°C. The formation of tricalcium phosphate from the neutralization of phosphoric acid with calcium carbonate in $\text{CaCO}_3 : \text{P}_2\text{O}_5$ ratio of 3 : 1 is incomplete.

Dibasic phosphate can be conveniently prepared by adding calcium carbonate to phosphoric acid in the molecular ratio of 2 : 1. The optimum concentrations of phosphoric acid are 0.02M and M at 5° and 30°C respectively, which give the maximum efficiency of precipitation of dicalcium phosphate when calcium carbonate is added to phosphoric acid in the molecular ratio of $\text{CaCO}_3 : \text{P}_2\text{O}_5$ as 2 : 1.

Introduction

Studies on the production of calcium phosphates have attracted the attention of several workers since the beginning of the 19th century. Piccard¹, Baer², Drevermann³, Becquerel⁴, Vohl⁵, Palmaer and Wiborgh⁶, Debray and Erlenmeyer⁷, Causse⁸, Millot⁹, Joly¹⁰ and Barille¹¹ reported the preparation of dicalcium phosphate, whilst Warington¹², Berzelius¹³, Withers and Field¹⁴, Gawalowsky¹⁵, Gaubert¹⁶, Berthelot¹⁷, Schlosing¹⁸ and Cornelius¹⁹ claimed to have obtained tricalcium phosphate. Nurse *et al.*²⁰ reported the formation of super alpha tricalcium phosphate (high temperature form). Dallemande *et al.*²¹ and other use the term 'alpha tricalcium phosphate' for hydroxyl apatite for which ca/p ratio is 1.5.

It has been observed by several workers that under certain conditions of concentration and temperature many definite molar species of mono, di and tri calcium phosphates or hydrates or their mixture may be formed as solid phases in contact with the solution. Among these preparations mention may be made of Vorbringer's²² $\text{CaHPO}_4 \cdot 1/6 \text{H}_2\text{O}$, which Brinbaum²³ found to be free from water.

Gerland²⁴, Raewsky²⁵ and Millot's⁹ $\text{CaHPO}_4 \cdot 1/2 \text{H}_2\text{O}$, Skey²⁶ and Delattre's²⁷ $\text{CaHPO}_4 \cdot 1 \frac{1}{2} \text{H}_2\text{O}$, Debray²⁸, Schulten²⁹, Chadelon³⁰ and Dallamagne and Melon's³¹ $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, Dusart and Pelouze's³² $\text{CaHPO}_4 \cdot 2 \frac{1}{12}\text{H}_2\text{O}$ and Barille's³³ $\text{CaHPO}_4 \cdot 4\text{H}_2\text{O}$.

Cameron and Seidell³⁴ have reported that tricalcium phosphate prepared by precipitation is impure and non-crystalline and a pure and crystalline product having $\text{CaO} : \text{P}_2\text{O}_5$ as 3 : 1 has not been prepared. According Hodge, Lefevre and Bale³⁴ the commercial tertiary phosphates are probably hydroxy apatites with more or less adsorbed phosphate resulting in the empirical formula approaching $\text{Ca}_3\text{P}_2\text{O}_8$. Bjerrum³⁵ also agrees that normal calcium phosphates are never precipitated from aqueous solutions. According to Jolibois and Spencer³⁶ tricalcium phosphate precipitated by adding phosphoric acid to an excess of lime adsorbs large amount of lime. Jolibois³⁷ mixed lime with different concentrations of phosphoric acid and reported the formation of compounds having $\text{CaO} : \text{P}_2\text{O}_5$ ratio of 2.84, 3.43, 3.45 and 4.30. Many workers have assumed tricalcium phosphate to be present in one or more of the following forms :

- (a) a solid solution of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$ ³⁸.
- (b) a mixture of mono and tri salts³⁹.
- (c) a mixture of tricalcium phosphate, dicalcium phosphate and lime⁴⁰.
- (d) a mixture of dicalcium phosphate and hydroxyapatite⁴¹.
- (e) a hydroxyapatite with more or less adsorbed phosphate ions resulting in empirical formula $\text{Ca}_3\text{P}_2\text{O}_8$ ⁴².
- (f) a solid solution containing calcium phosphate in which a further uptake of calcium must be accompanied by entry of hydroxyl ions^{43, 44}.

In order to obtain a detailed knowledge about the nature of the products formed by the neutralization of phosphoric acid with calcium carbonate at 5° and 30°C, a systematic investigation has been made. Moreover, the optimum conditions at which the maximum yield of calcium phosphates can be obtained have been worked out.

Experimental

Extra pure phosphoric acid and B. D. H. quality of calcium carbonate were added in these experiments. 25 ml standard solutions of phosphoric acid of different concentrations i.e. 5M, M, 0.2M and 0.02M were taken in 250 ml Jena glass bottles. Three sets of each concentration were taken and calcium carbonate was added in the molecular ratio of $\text{CaCO}_3 : \text{P}_2\text{O}_5$ as 1 : 1, 2 : 1 and 3 : 1.

While adding calcium carbonate the solutions were vigorously shaken and the rise of temperature due to the heat of reaction was noted down in every case. The contents were then shaken in a mechanical shaker for one hour and left for 24 hours in a bath at 30°C. For 5°C, a Philips refrigerator was used whose temperature was constantly maintained. Next day the solid was drained by suction in a sintered crucible and the filtrate was collected. The solid was thoroughly washed with acetone and ether. It was air dried. The amounts of the solid residues were weighed. A portion of the solid was dissolved in dilute hydrochloric acid and the solution made upto a definite volume. Aliquot portions of the solutions were utilized for the analysis of the ingredients. Electric conductivity and pH measurements of the filtrates were also carried out at 30°C.

Observations

TABLE 1

Concen- tration of phosphoric acid	Molecular ratio of CaCO_3 : P_2O_5	Initial specific conductivity in mhos $\times 10^{-3}$	Specific conductivity of filtrate in mhos	Initial pH of the acid	pH of filtrate
5M	1 : 1	180.3	42.24×10^{-3}	0.40	2.00
	2 : 1		11.87×10^{-4}		4.55
	3 : 1		4.82×10^{-4}		8.30
M	1 : 1	48.8	24.73×10^{-3}	0.80	2.45
	2 : 1		7.81×10^{-4}		5.15
	3 : 1		3.33×10^{-4}		8.15
0.2M	1 : 1	14.68	10.05×10^{-3}	1.40	3.10
	2 : 1		5.23×10^{-4}		5.75
	3 : 1		2.55×10^{-4}		8.00
0.02M	1 : 1	3.27	3.08×10^{-3}	2.35	3.95
	2 : 1		2.83×10^{-4}		6.35
	3 : 1		1.26×10^{-4}		7.70

TABLE 2

The solid residues obtained after mixing calcium carbonate and phosphoric acid at 5° and 30°C respectively have the following compositions : Temperature 5°C

Concen- tration of phosphoric acid	Molecular ratio of CaCO_3 : P_2O_5	Rise in tempera- ture in °C	P_2O_5 %	CaO %	Nature of residue
5M	1 : 1	14.5	53.01	41.80	CaHPO_4
	2 : 1	16.0	52.26	42.11	CaHPO_4
	3 : 1	16.5	45.02	48.89	$2.75 \text{ CaO} : \text{P}_2\text{O}_5$
M	1 : 1	6.0	48.06	38.11	$\text{CaHPO}_4 \cdot \frac{3}{4} \text{H}_2\text{O}$
	2 : 1	7.0	47.77	37.98	$\text{CaHPO}_4 \cdot \frac{3}{4} \text{H}_2\text{O}$
	3 : 1	7.5	42.53	47.11	$2.81 \text{ CaO} : \text{P}_2\text{O}_5$
0.02M	1 : 1	3.5	—	—	No residue obtained
	2 : 1	3.5	46.21	36.55	$\text{CaHPO}_4 \cdot \text{H}_2\text{O}$
	3 : 1	4.0	40.25	44.44	$2.80 \text{ CaO} : \text{P}_2\text{O}_5$
0.02M	1 : 1	1.0	—	—	No residue obtained
	2 : 1	1.5	41.83	33.11	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
	3 : 1	1.5	37.93	42.04	$2.80 \text{ CaO} : \text{P}_2\text{O}_5$
5M	1 : 1	10.5	52.93	42.05	CaHPO_4
	2 : 1	11.5	52.17	41.88	CaHPO_4
	3 : 1	12.0	45.13	49.10	$2.76 \text{ CaO} : \text{P}_2\text{O}_5$
M	1 : 1	4.0	49.70	40.03	$\text{CaHPO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$
	2 : 1	4.5	48.90	40.00	$\text{CaHPO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$
	3 : 1	4.5	43.02	47.80	$2.81 \text{ CaO} : \text{P}_2\text{O}_5$
0.02M	1 : 1	2.0	—	—	No residue obtained
	2 : 1	2.0	48.12	38.70	$\text{CaHPO}_4 \cdot \frac{3}{4} \text{H}_2\text{O}$
	3 : 1	2.5	41.30	47.40	$2.91 \text{ CaO} : \text{P}_2\text{O}_5$
0.02M	1 : 1	0.0	—	—	No residue obtained
	2 : 1	0.5	44.00	35.10	$\text{CaHPO}_4 \cdot \frac{3}{2} \text{H}_2\text{O}$
	3 : 1	0.5	39.20	43.30	$1.80 \text{ CaO} : \text{P}_2\text{O}_5$

TABLE 3

Concen- tration of phosphoric acid	Molecular ratio of CaCO_3 : P_2O_5	Amount of CaCO_3 added in gms	Amount of product formed in gms at 5°C	Amount of product formed in gms at 30°C
5M	1 : 1	6.2500	4.8388	4.7996
	2 : 1	12.5000	15.6114	15.0002
	3 : 1	18.7500	19.4016	19.3112
	1 : 1	1.2500	0.7726	0.7576
	2 : 1	2.5000	3.4386	3.2024
	3 : 1	3.7500	4.0870	3.9988
0.2M	1 : 1	0.2500	—	—
	2 : 1	0.5000	0.7144	0.6208
	3 : 1	0.7500	0.8432	0.814
0.02M	1 : 1	0.0250	—	—
	2 : 1	0.0500	0.0738	0.0678
	3 : 1	0.0750	0.0892	0.0880

TABLE 4

Concen- tration of phosphoric acid	Molecular ratio of CaCO_3 : P_2O_5	Percentage of P_2O_5 used up		Percentage efficiency of precipita- tion of dicalcium phosphate	
		5°C	30°C	5°C	30°C
5M	1 : 1	29.40	29.02	56.92	56.47
	2 : 1	93.56	90.65	91.83	88.23
	3 : 1	99.92	99.95	—	—
	1 : 1	21.29	21.59	41.34	41.79
	2 : 1	94.18	89.73	92.00	88.34
	3 : 1	99.05	98.66	—	—
0.2M	1 : 1	—	—	—	—
	2 : 1	94.64	85.67	92.77	83.06
	3 : 1	97.30	95.98	—	—
0.02M	1 : 1	—	—	—	—
	2 : 1	88.50	85.68	85.81	83.26
	3 : 1	97.28	98.89	—	—

Discussion

The experimental results show that there is a gradual fall in the electric conductivity, when calcium carbonate is added to phosphoric acid in the molecular ratio for $\text{CaCO}_3 : \text{P}_2\text{O}_5$ as 1 : 1, 2 : 1 and 3 : 1. The conductivity of the filtrates is always maximum when calcium carbonate is added to phosphoric acid in the ratio of 1 : 1 and minimum when added in the ratio of 3 : 1. Thus, it is clearly shown that the maximum number of ions are removed from solutions when calcium carbonate is added to phosphoric acid in the $\text{CaCO}_3 : \text{P}_2\text{O}_5$ ratio of 3 : 1.

The pH determinations indicate that the hydrogen ion concentration decreases with the increasing amounts of calcium carbonate added. From these results it seems that hydrogen ions are continuously adsorbed on the surface of the solid. The uptake of hydrogen ions is directly proportional to the amount of calcium

carbonate added. It has been observed that the pH of the solutions of CaCO_3 : P_2O_5 of 3 : 1 is always on the alkaline side indicating that there is more of lime than P_2O_5 remaining in the solutions.

It would naturally be expected that the successive addition of calcium carbonate to phosphoric acid in the molecular ratio of CaCO_3 : P_2O_5 as 1 : 1, 2 : 1 and 3 : 1, mono, di and tri salts should be formed, but from the obtained experimental results it is clear that quite a different salt of affairs exists in the system. On adding calcium carbonate to phosphoric acid in the CaCO_3 : P_2O_5 ratio of 1 : 1, it has been found that at 0.2M and 0.02M acid concentrations the whole of the added calcium carbonate has dissolved. It is remarkable that the solid residues have the composition of dicalcium phosphate instead of monocalcium phosphate. The ratio of CaO : P_2O_5 in these solids is always 2 : 1. It appears that monocalcium phosphate is formed in the solutions, but in concentrated solutions it breaks up into dicalcium phosphate and free phosphoric acid.

Dicalcium phosphate with different degrees of hydration is invariably obtained when calcium carbonate and phosphoric acid are mixed in the molecular ratio of CaCO_3 : P_2O_5 of 2 : 1. With 0.02M concentration of the acid the solid formed is dihydrated dicalcium phosphate at 5°C. From the experimental results it appears that with the decrease in the concentration of the acid the solid residue has a tendency to pass from anhydrous to hydrated form. The compounds formed with the same concentration of the acid at 5° and 30°C differ in their degrees of hydration. It can be concluded that the degree of hydration of the solid depends upon the temperature of the reaction and the concentration of the acid. The percentage amount of P_2O_5 that is used up in the reaction is always greater at 5°C than at 30°C with the same concentration of the acid. It appears that the neutralization of phosphoric acid with calcium carbonate in the ratio of CaCO_3 : P_2O_5 as 2 : 1 is more facilitated at 5°C than at 30°C.

From the experiments in which calcium carbonate was added to phosphoric acid in the CaCO_3 : P_2O_5 ratio of 3 : 1 it has been observed that the solid residues is neither pure dicalcium phosphate nor tricalcium phosphate but a mixture of the two. It is indicated from these results that the formation of tricalcium phosphate from the neutralization of phosphoric acid with calcium carbonate in the ratio of 3 : 1 is incomplete. It has been observed that the percentage removal of P_2O_5 from the solution is always greater when calcium carbonate is added to phosphoric acid in the ratio of 3 : 1 than with 1 : 1 or 2 : 1.

It is evident from the results that dibasic phosphate can be conveniently prepared by adding calcium carbonate to phosphoric acid in the molecular ratio of 2 : 1. The optimum concentration of phosphoric acid which gives the maximum efficiency of precipitation of dicalcium phosphate when calcium carbonate is added in the ratio of CaCO_3 : P_2O_5 as 2 : 1 is 0.02M at 5°C and M acid concentration at 30°C. It appears that this method of neutralization of phosphoric acid by calcium carbonate may serve as a cheap method for the manufacture of dicalcium phosphate which has been found to be as effective in crop production as superphosphate. Moreover, dicalcium phosphate is slightly alkaline and much richer in P_2O_5 content than superphosphate, whereas superphosphate has marked acidic properties and in some cases the pH of the soil has gone down upto 1.5, requiring more lime for cultivation. Dihydrated dicalcium phosphate is a valuable plant food and is also fed to animals especially when suffering from calving difficulties.

References

1. Piccard, J. *Schweiz. Polyt. Zeit.*, **11**, 83, 1866.
2. Baer, W. *Pogg. Ann.*, **75**, 152, 1847.
3. Drevermann, A. *Liebig's Ann.*, **87**, 120, 1853.
4. Becquerel, A. C. *Compt. Rend.*, **34**, 573, 1852.
5. Vohl, H. *Liebig's Ann.*, **88**, 114, 1853.
6. Palmaer, W. and Wiborgh, J. *Chem. Trade Journ.*, **67**, 541, 1920.
7. Debray, J. H. and Erlenmeyer. *Ann. Chim. Phys.*, **11** (1), 114, 1860.
8. Causse, H. E. *J. Pharm. Chim.*, **21** (5), 244, 1890.
9. Millot, A. *Bull. Soc. Chim.*, **5** (3), 154, 1891.
10. Joly, J. *Compt. Rend.*, **97**, 1480, 1883.
11. Berille, A. *Pharm. Centrh.*, **39**, 24, 1898.
12. Warington, R. *Journ. Chem. Soc.*, **19**, 296, 1866.
13. Berzelius, J. J. *Liebig's Ann.*, **53**, 246, 1845.
14. Withers, W. A. and Field, A. L. *Journ. Amer. Chem. Soc.*, **37**, 1091, 1915.
15. Gawalowsky. *Oester. Chem. Ztg.*, **2**, 412, 1899.
16. Gaubert, P. *Compt. Rend.*, **147**, 1115, 1922.
17. Berthelot, M. *Ann. Chim. Phys.*, **11** (6), 1887.
18. Schlosing. *Compt. Rend.*, **131**, 149, 1900.
19. Cornelius. *J. Pharm. Chim.*, **57**, 13-29, 1886.
20. Nurse, R. W., Welch, J. H. and Gutt, W. *Nature*, **182**, 1230, 1958.
21. Dallemagne, M. J., Brasseur, H. and Melon, J. *Bull. Soc. Chim. France, Mises au point D*, 138-45, 1949.
22. Vorbringer, G. *Zeit. Anal. Chem.*, **9**, 457, 1870.
23. Brinbaum, K. *Zeit. Chem.*, **7** (2), 131, 1871.
24. Gerland, B. W. *Chem. News*, **20**, 268, 1870.
25. Raewsky, M. *Compt. Rend.*, **26**, 205, 1848.
26. Skey, W. *Chem. News*, **25**, 258, 1872.
27. Delattre, C. *Ann. Chim. Phys.*, **61** (3), 424, 1860.
28. Debray, J. H. *Bull. Soc. Chim.*, **35** (2), 358, 1881.
29. Schulten, A. D. *Bull. Soc. Min.*, **26**, 11, 1903; **27**, 109, 1905.
30. Chandelon, T. *Brit. Pat. No.* 13842, 1893.
31. Dallemagne, M. J. and Melon, J. *Bull. Soc. Chim. Belges.*, **55**, 38, 1946.
32. Dusart, L. and Pelouze, J. *Compt. Rend.*, **66**, 1327, 1868.
33. Cameron, F. K. and Seidell, A. *Journ. Amer. Chem. Soc.*, **27**, 1503, 1905.
34. Hodge, H. C., Lefevre, M. L. and Bale, W. F. *Ind. Eng. Chem. Anal. Ed.*, **10**, 156-61, 1938
35. Bjerrum, N. Selected Papers, edited by Friends and Coworkers, Copenhagen, 1949, 1936.
36. Jolibois, P. and Spencer, J. M. *Compt. Rend.*, **181**, 36-37, 1925.
37. Jolibois, P. *Compt. Rend.*, **169**, 1161-63, 1919.
38. Cameron, F. K. and Bell, J. M. *J. Am. Chem. Soc.*, **27**, 1512, 1905.
39. Wendt. and Clarke. *J. Am. Chem. Soc.*, **45**, 881, 1923.
40. Burns and Henderson. *Biochem. J.*, **29**, 2385, 1935.
41. Scheele et al. *Z. Electrochem.*, **38**, 633, 1932.
42. Hodge et al. *Ind. Eng. Chem. Anal. Ed.*, **10**, 156, 1938.
43. Crowther. Quoted from *Chem. Ind.*, **31**, 1931 and 1949.
44. Eisenberger, S. *Chem. Revs.*, **26**, 257-296, 1940.

Some Expansion Formulae for H-function—III

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Abstract

In this paper, we have established some expansion formulae for H-function. These expansions are further generalized by Laplace transform techniques. The results obtained are of a very general character and those for H-function already given by author [1] and for Meijer's G-function given by Wimp and Luke [12] follow as particular cases.

1. Introduction : Fox [8, p. 408], introduced the H-function in the form of Mellin-Barnes type integral, which has been symbolically denoted by Gupta and Jain [9].

$$(1.1) \quad H_{p, q}^{m, n} \left[x \middle| \begin{matrix} \{(a_p, \alpha_p)\} \\ \{(b_q, \beta_q)\} \end{matrix} \right] = \frac{1}{2\pi i} \int_T \frac{\prod_{j=1}^m \Gamma(b_j - \beta_j s) \prod_{j=1}^n \Gamma(1 - a_j + \alpha_j s)}{\prod_{j=m+1}^q \Gamma(1 - b_j + \beta_j s) \prod_{j=n+1}^p \Gamma(a_j - \alpha_j s)} x^s ds,$$

where $\{(f_r, \gamma_r)\}$ stands for the set of the parameters $(f_1, \gamma_1), \dots, (f_r, \gamma_r)$; x is not equal to zero and empty product is interpreted as unity; p, q, m and n are integers satisfying $1 \leq m \leq q, 0 \leq n \leq p$; α_j ($j = 1, 2, \dots, p$), β_j ($j = 1, 2, \dots, q$) are positive numbers and a_j ($j = 1, 2, \dots, p$), b_j ($j = 1, 2, \dots, q$) are complex numbers such that no pole of $\Gamma(b_h - \beta_h s)$ ($h = 1, 2, \dots, m$) coincides with any pole of $\Gamma(1 - a_i + \alpha_i s)$ ($i = 1, 2, \dots, n$) i.e.

$$(1.2) \quad \alpha_i(b_h + \nu) \neq \beta_h(a_i - \eta - 1)$$

$$(\nu, \eta = 0, 1, \dots; h = 1, 2, \dots, m; i = 1, 2, \dots, n).$$

According to Braaksma [4, p. 278], H-function makes sense and defines an analytic function of x in the following two cases:

(a) If $\mu > 0, x \neq 0$

where

$$(1.3) \quad \mu = \sum_1^q (\beta_j) - \sum_1^p (\alpha_j)$$

(b) If $\mu = 0, 0 < |x| < \beta^{-1}$

where

$$(1.4) \quad \beta = \prod_{j=1}^p (\alpha_j)^{a_j} \prod_{j=1}^q (\beta_j)^{-\beta_j}.$$

From [4, p. 276 (6·5)], we have

$$(1·5) \quad H_{p, q}^{m, n} \left[x \begin{matrix} \{(a_p, \alpha_p)\} \\ \{(b_q, \beta_q)\} \end{matrix} \right] = 0 \text{ (} |x|^\alpha \text{ for small } x \text{.}$$

where $\sum_1^q (\beta_j) - \sum_1^p (\alpha_j) \geq 0$ and $\alpha = Re\left(\frac{b_h}{\beta_h}\right)$ ($h = 1, 2, \dots, m$).

From [4, p. 246 (2·16)], we get

$$(1·6) \quad H_{p, q}^{m, n} \left[x \begin{matrix} \{(a_p, \alpha_p)\} \\ \{(b_q, \beta_q)\} \end{matrix} \right] = 0 \text{ (} |x|^\beta \text{ for large } x \text{,}$$

where $\sum_1^q (\beta_j) - \sum_1^p (\alpha_j) > 0$, $\sum_1^n (\alpha_j) - \sum_{n+1}^p (\alpha_j) + \sum_1^m (\beta_j) - \sum_{m+1}^q (\beta_j) \equiv \lambda > 0$,
 $|\arg x| < \frac{1}{2}\lambda\pi$ and $\beta = Re\left(\frac{a_i - 1}{a_i}\right)$ ($i = 1, 2, \dots, n$).

The behaviour of H-function for large x has been considered by Braaksma at full length. He has considered different sets of conditions of convergence for the integral given by (1·1). However, we restrict ourselves to above conditions of validity.

In what follows, for the sake of brevity $\Gamma(d_s)$ stands for $\prod_{j=1}^s \Gamma(d_j)$.

2. In this section, we state the known results which will be used in our present work.

An integral due to Gupta and Jain [9, 6(a)]

$$(2·1) \quad \int_0^\infty x^{\eta-1} H_{p, q}^{m, n} \left[zx^\sigma \begin{matrix} \{(a_p, \alpha_p)\} \\ \{(b_q, \beta_q)\} \end{matrix} \right] G_{r, l}^{k, f} \left[sx \begin{matrix} c_1, \dots, c_r \\ d_1, \dots, d_l \end{matrix} \right] dx \\ = \frac{1}{s^\eta} H_{p+l, q+r}^{m+f, n+k} \left[\frac{z}{s^\sigma} \begin{matrix} \{(a_n, \alpha_n)\}, \{(1-d_l-\eta, \sigma)\}, (a_{n+1}, \alpha_{n+1}), \dots, (a_p, \alpha_p) \\ \{(b_m, \beta_m)\}, \{(1-c_r-\eta, \sigma)\}, (b_{m+1}, \beta_{m+1}), \dots, (b_q, \beta_q) \end{matrix} \right]$$

provided that $Re[\eta + \sigma b_h | \beta_h + d_i] > 0$ ($h = 1, 2, \dots, m$; $i = 1, 2, \dots, k$),

$$Re\left[\eta + (c_j - 1) + \sigma \frac{(a_{h'} - 1)}{a_{h'}}\right] < 0 \quad (j = 1, 2, \dots, f; h' = 1, 2, \dots, n), \quad \lambda > 0, \quad \sigma > 0,$$

$|\arg z| < \frac{1}{2}\lambda\pi$, $\mu > 0$ and $|\arg s| < \frac{1}{2}\mu\pi$ where $\mu = 2k + 2f - l - r$

and $\lambda = \sum_1^q (\beta_j) - \sum_{m+1}^q (\beta_j) + \sum_1^n (\alpha_j) - \sum_{n+1}^p (\alpha_j)$.

$$(2·2) \quad e^{-px} \equiv G_{0, 1}^{1, 0} (px | 0).$$

Properties of H-function given by Gupta and Jain [9]

$$(2·3) \quad H_{p, q}^{m, n} \left[x \begin{matrix} \{(a_p, \alpha_p)\} \\ \{(b_q, \beta_q)\} \end{matrix} \right] \equiv c H_{p, q}^{m, n} \left[x^c \begin{matrix} \{(a_p, ca_p)\} \\ \{(b_q, c\beta_q)\} \end{matrix} \right], \text{ where } c > 0,$$

$$(2.4) \quad H_{p, q}^{m, n} \left[x^{-1} \middle| \begin{matrix} \{(a_p, \alpha_p)\} \\ \{(b_q, \beta_q)\} \end{matrix} \right] \equiv H_{q, p}^{n, m} \left[x \middle| \begin{matrix} \{(1 - b_q, \beta_q)\} \\ \{(1 - a_p, \alpha_p)\} \end{matrix} \right],$$

$$(2.5) \quad H_{p, q}^{m, n} \left[x \middle| \begin{matrix} (a_1, \alpha_1), \dots, (a_p, \alpha_p) \\ (b_1, \beta_1), \dots, (b_{q-1}, \beta_{q-1}), (a_1, \alpha_1) \end{matrix} \right] \\ \equiv H_{p-1, q-1}^{m, n-1} \left[x \middle| \begin{matrix} (a_2, \alpha_2), \dots, (a_p, \alpha_p) \\ (b_1, \beta_1), \dots, (b_{q-1}, \beta_{q-1}) \end{matrix} \right],$$

provided $n \geq 1$ and $m < q$.

The relation between G -and H -functions :

$$(2.6) \quad H_{p, q}^{m, n} \left[x \middle| \begin{matrix} \{(a_p, 1)\} \\ \{(b_q, 1)\} \end{matrix} \right] \equiv G_{p, q}^{m, n} \left(x \middle| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right).$$

The relation between H -function and Wright's generalized hypergeometric function [13, p. 287]

$$(2.7) \quad H_{p, q+1}^{1, p} \left[x \middle| \begin{matrix} \{(1 - a_p, \alpha_p)\} \\ (0, 1), \{(1 - b_q, \beta_q)\} \end{matrix} \right] \equiv \sum_{r=0}^{\infty} \frac{\prod_{j=1}^p \Gamma(a_j + \alpha_j s) (-x)^r}{\prod_{j=1}^q \Gamma(b_j + \beta_j s) r!} \\ \equiv {}_p\psi_q \left[\begin{matrix} \{(a_p, \alpha_p)\} \\ \{(b_q, \beta_q)\} \end{matrix}; -x \right].$$

3. Here we establish some integrals which are required in the development of the present work.

$$(3.1) \quad \int_0^\infty x^{\rho-1} e^{-x} L_{\beta}^{(\alpha)}(x) H_{p, q}^{m, n} \left[z^{\delta} x^\delta \middle| \begin{matrix} \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\} \end{matrix} \right] dx \\ = \frac{1}{\beta!} H_{p+2, q+1}^{m+1, n+1} \left[z^\delta \middle| \begin{matrix} (1 - \rho, \delta), \{(a_p, \delta \alpha_p)\}, (\alpha - \rho + 1, \delta) \\ (\alpha + \beta - \rho + 1, \delta), \{(b_q, \delta \beta_q)\} \end{matrix} \right],$$

where δ is a positive number and provided $Re\left(\rho + \frac{bj}{\beta_j}\right) > 0$ ($j = 1, 2, \dots, m$),

$$\sum_1^m (\beta_j) - \sum_{m+1}^q (\beta_j) + \sum_1^n (\alpha_j) - \sum_{n+1}^p (\alpha_j) \equiv \lambda > 0, |\arg z^\delta| < \frac{1}{2} \lambda \pi.$$

Proof: Expressing H -function on the left hand side as Mellin-Barnes type integral (1.1), changing the order of integration, which is justifiable due to the absolute convergence of the integrals involved in the process, it reduces to

$$\frac{1}{2\pi i} \int \frac{\prod_{j=1}^m \Gamma(b_j - \delta \beta_j \xi)}{\prod_{j=m+1}^q \Gamma(1 - b_j + \delta \beta_j \xi)} \frac{\prod_{j=1}^n \Gamma(1 - a_j + \delta \alpha_j \xi)}{\prod_{j=n+1}^p \Gamma(a_j - \delta \alpha_j \xi)} z^{\delta \xi} d\xi \int_0^\infty x^{\rho + \delta \xi - 1} e^{-x} L_{\beta}^{(\alpha)}(x) dx,$$

evaluating the inner integral with the help of [3, p. 292(i)], we get

$$\frac{1}{\beta!} \frac{1}{2\pi i} \int \frac{\prod_{j=1}^m \Gamma(b_j - \delta \beta_j \xi) \prod_{j=1}^n \Gamma(1 - a_j + \delta \alpha_j \xi) \Gamma(\rho + \delta \xi) \Gamma(1 + \beta + \alpha - \rho - \delta \xi)}{T \prod_{j=m+1}^q \Gamma(1 - b_j + \delta \beta_j \xi) \prod_{j=n+1}^p \Gamma(a_j - \delta \alpha_j \xi) \Gamma(1 + \alpha - \rho - \delta \xi)} z^{\delta \xi} d\xi,$$

now using (1.1), the definition of H-function, we obtain the result.

$$(3.2) \quad \int_0^\infty x^{-\rho} e^{-\lambda x} H_{p, q}^{m, n} \left[\begin{matrix} \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\} \end{matrix} \middle| z^{\delta x \delta} \right] dx \\ = \frac{1}{\lambda^{1-\rho}} H_{p+1, q}^{m, n+1} \left[\begin{matrix} (\rho, \delta) \{(a_p, \delta \alpha_p)\} \\ \{\{(b_q, \delta \beta_q)\}\} \end{matrix} \middle| \lambda^{\delta} \right],$$

where δ is a positive number and provided $[1 - \rho + b_j | \beta_j] > 0$ ($j = 1, 2, \dots, m$),
 $|\arg \lambda| < \frac{1}{2} \pi$,

$$\delta \left[\sum_1^m (\beta_j) - \sum_{m+1}^q (\beta_j) + \sum_1^n (\alpha_j) - \sum_{n+1}^p (\alpha_j) \right] \equiv \mu > 0, |\arg z^\delta| < \frac{1}{2} \mu \pi.$$

The value of the integral (3.2) can easily be established with the help of (2.2) and (2.1).

Now, let $\phi(\lambda) = \int_0^\infty e^{-\lambda t} f(t) dt$

that is $\phi(\lambda) \doteqdot f(t)$

and, let $f(t) = t^{-\sigma} H_{p, q+1}^{m, n} \left[\begin{matrix} \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\}, (\sigma, \delta) \end{matrix} \middle| z^\delta t^\delta \right]$,

then, using (2.2) and (2.1) we get

$$(3.3) \quad \lambda^{\sigma-1} H_{p, q}^{m, n} \left[\begin{matrix} z^\delta \\ \lambda^\delta \end{matrix} \middle| \begin{matrix} \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\} \end{matrix} \right] \doteqdot t^{-\sigma} H_{p, q+1}^{m, n} \left[\begin{matrix} \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\}, (\sigma, \delta) \end{matrix} \middle| z^\delta t^\delta \right],$$

where δ is a positive number and provided $Re[1 - \sigma + b_j | \beta_j] > 0$ ($j = 1, 2, \dots, m$),

$$\delta \left[\sum_1^m (\beta_j) - \sum_{m+1}^q (\beta_j) + \sum_1^n (\alpha_j) - \sum_{n+1}^p (\alpha_j) - 1 \right] \equiv \phi > 0,$$

$$|\arg z^\delta| < \frac{1}{2} \phi \pi, |\arg \lambda| < \frac{1}{2} \pi.$$

4. In this section, we establish a Lemma and use it in finding expansions.

Assumptions :

(i) Let δ be a positive number ; p, q, m and n are positive integers such that $1 \leq m \leq q+1, 0 \leq n \leq p$.

(ii) Let $\sum_1^q (\beta_j) - \sum_1^p (\alpha_j) > 0, z^{\delta w \delta} \neq 0 ; \sum_1^q (\beta_j) - \sum_1^p (\alpha_j) = 0, 0 < |z^{\delta w \delta}| < \beta^{-1}$

where $\beta = \prod_{j=1}^p (\alpha_j)^{\alpha_j} \prod_{j=1}^q (\beta_j)^{-\beta_j} \delta^{(p-q)\delta}$; $\sum_1^q (\beta_j) - \sum_1^p (\alpha_j) - \delta > 0$, $z^\delta \neq 0$;

$\sum_1^q (\beta_j) - \sum_1^p (\alpha_j) - \delta = 0$, $0 < |z^\delta| < \alpha^{-1}$ where $\alpha = \prod_{j=1}^p (\alpha_j)^{\alpha_j} \prod_{j=1}^q (\beta_j)^{-\beta_j} \delta^{(p-q+1)\delta}$

(iii) Let $\delta \left[\sum_1^m (\beta_j) - \sum_{m+1}^q (\beta_j) + \sum_1^n (\alpha_j) - \sum_{n+1}^p (\alpha_j) \right] \equiv \lambda > 0$, $|\arg z^\delta w^\delta| < \frac{1}{2}\lambda\pi$:

$$\delta \left[\sum_1^m (\beta_j) - \sum_{m+1}^q (\beta_j) + \sum_1^n (\alpha_j) - \sum_{n+1}^p (\alpha_j) + 1 \right] \equiv \phi > 0, |\arg z^\delta| < \frac{1}{2}\phi\pi;$$

$$Re \left(\mu + \alpha + \frac{b_j}{\beta_j} \right) > -1 \quad (j = 1, 2, \dots, m), Re(\alpha) > -1.$$

(iv) Let $\alpha_i(b_h + \nu) \neq \beta_h(a_i - \eta - 1)$, $(b_h + \nu) \neq \beta_h(-\mu - \alpha - \eta - 1)$,

$$(b_h + \nu) \neq \beta_h(-\mu - \eta - 1)$$

$$(\nu, \eta = 0, 1, \dots; h = 1, 2, \dots, m; i = 1, 2, \dots, n)$$

then

$$(4.1) \quad w^\mu H_{p,q}^{m,n} \left[z^{\delta w^\delta} \middle| \begin{matrix} \{(a_p, \delta a_p)\} \\ \{(b_q, \delta b_q)\} \end{matrix} \right]$$

$$= \frac{1}{\Gamma(\alpha+1)} \sum_{N=0}^{\infty} \frac{(-1)^N}{N!} {}_1F_1 \left[\begin{matrix} -N; W \\ \alpha+1 \end{matrix} \right] H_{p+2, q+1}^{m, n+2} \left[z \left| \begin{matrix} (-\mu-\alpha, \delta), (-\mu, \delta), \{(a_p, \delta a_p)\} \\ \{(b_q, \delta b_q)\}, (N-\mu, \delta) \end{matrix} \right. \right]$$

Proof: To prove (4.1), let

$$(4.2) \quad w^\mu H_{p,q}^{m,n} \left[z^{\delta w^\delta} \middle| \begin{matrix} \{(a_p, \delta a_p)\} \\ \{(b_q, \delta b_q)\} \end{matrix} \right] = \sum_{N=0}^{\infty} c_N L_N^{(\alpha)}(w).$$

Here $L_N^{(\alpha)}(w)$ is a Laguerre polynomial. Equation (4.2) is valid since the left hand side, in view of (2.3), is a function of w and is continuous and of bounded variation in the interval $(0, \infty)$.

Multiplying both the sides of (4.2) by $w^\alpha e^{-w} L_\nu^{(\alpha)}(w)$, integrating with respect to w from 0 to ∞ , interchanging the order of summation and integration on the right hand side, which is permissible due to [5, p. 500], we get

$$\begin{aligned} & \int_0^\infty w^{\mu+\alpha} e^{-w} L_\nu^{(\alpha)}(w) H_{p,q}^{m,n} \left[z^{\delta w^\delta} \middle| \begin{matrix} \{(a_p, \delta a_p)\} \\ \{(b_q, \delta b_q)\} \end{matrix} \right] dw \\ &= \sum_{N=0}^{\infty} c_N \int_0^\infty w^\alpha e^{-w} L_N^{(\alpha)}(w) L_\nu^{(\alpha)}(w) dw, \end{aligned}$$

using (3.1) on the left hand side and orthogonality property of Laguerre polynomials [3, p. 292(2)], [3, p. 293(3)] on the right hand side, we obtain

$$(4 \cdot 3) \quad c_v = \frac{1}{\Gamma(u+v+1)} H_{p+2, q+1}^{m+1, n+1} \left[z^\delta \begin{matrix} (-\alpha - \mu, \delta), \{(a_p, \delta \alpha_p)\}, (-\mu, \delta) \\ (\nu - \mu, \delta), \{(b_q, \delta \beta_q)\} \end{matrix} \right].$$

Now (4.2) with the help of (4.3), reduces to

$$(4 \cdot 4) \quad w^\mu H_{p, q}^{m, n} \left[z^{\delta w \delta} \begin{matrix} \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\} \end{matrix} \right] \\ = \sum_{N=0}^{\infty} \frac{1}{\Gamma(\alpha + N + 1)} L_N^{(\alpha)}(w) H_{p+2, q+1}^{m+1, n+1} \left[z^\delta \begin{matrix} (-\alpha - \mu, \delta), \{(a_p, \delta \alpha_p)\}, (-\mu, \delta) \\ (N - \mu, \delta), \{(b_q, \delta \beta_q)\} \end{matrix} \right].$$

On the right hand side, using the identity

$$(4 \cdot 5) \quad H_{p+2, q+1}^{m+1, n+1} \left[z^\delta \begin{matrix} (-\alpha - \mu, \delta), \{(a_p, \delta \alpha_p)\}, (-\mu, \delta) \\ (N - \mu, \delta), \{(b_q, \delta \beta_q)\} \end{matrix} \right] \\ = (-1)^N H_{p+2, q+1}^{m, n+2} \left[z^\delta \begin{matrix} (-\alpha - \mu, \delta), (-\mu, \delta), \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\}, (N - \mu, \delta) \end{matrix} \right]$$

(which is apparent from the definition of H-function) and expressing the Laguerre polynomial in terms of hypergeometric function [11, p. 200(1)], we get the result (4.1).

Theorem 1

Assumptions :

(i) Let p, q, r, s, t, u, m and n be positive integers such that $1 \leq m \leq q+s$, $0 \leq n \leq p$, $1 \leq m \leq q+u+1$ and δ is a positive number.

(ii) Let none of the following quantities be negative integers

$$-c_j - \mu \quad (j = 1, 2, \dots, r), F_j - 1 \quad (j = 1, 2, \dots, u).$$

(iii) Let $\sum_1^q (\beta_j) - \sum_1^p (\alpha_j) + s - r > 0$ when $z^{\delta w \delta} \neq 0$; $\sum_1^q (\beta_j) - \sum_1^p (\alpha_j) + s - r = 0$,

when $0 < |z^{\delta w \delta}| < \beta^{-1}$ where $\beta = \delta^{(p+r-q-s)\delta} \prod_{j=1}^p (\alpha_j)^{\alpha_j} \prod_{j=1}^q (\beta_j)^{-\beta_j}$;

$\sum_1^q (\beta_j) - \sum_1^p (\alpha_j) + (u - t) > 0$ when $z^\delta \neq 0$; $\sum_1^q (\beta_j) - \sum_1^p (\alpha_j) + u - t = 0$

when $0 < |z^\delta| < \alpha^{-1}$ where $\alpha = \delta^{(p+t-q-u)\delta} \prod_{j=1}^p (\alpha_j)^{\alpha_j} \prod_{j=1}^q (\beta_j)^{-\beta_j}$.

(iv) Let $\delta \left[\sum_1^m (\beta_j) - \sum_{m+1}^q (\beta_j) + \sum_1^n (\alpha_j) - \sum_{n+1}^p (\alpha_j) + r - s \right] \equiv \lambda > 0$, $|\arg z^{\delta w \delta}| < \frac{1}{2}\pi$,

$\delta \left[\sum_1^m (\beta_j) - \sum_{m+1}^q (\beta_j) + \sum_1^n (\alpha_j) - \sum_{n+1}^p (\alpha_j) + t - u \right] \equiv \phi > 0$, $|\arg z^\delta| < \frac{1}{2}\phi\pi$

(v) Let $\alpha_i(b_h + \nu) \neq \beta_h(a_i - \eta - 1)$, $(b_h + \nu) \neq \beta_h(-f_k - \mu - \eta)$,
 $(b_h + \nu) \neq \beta_h(-\mu - \eta - 1)$, $(b_h + \nu) \neq \beta_h(c_g - \eta - 1)$
 $(\nu, \eta = 0, 1, \dots; h = 1, 2, \dots, m; i = 1, 2, \dots, n; k = 1, 2, \dots, t; g = 1, 2, \dots, r)$.

(vi) Let $r+u+1 = s+t$.

(vii) Let $\sum_{j=1}^s d_j - \sum_{j=1}^r c_j + \sum_{j=1}^u F_j - \sum_{j=1}^t f_j - 2b_h/\beta_h < (s-r)(1-\mu) - \frac{1}{2}$
 $(1 - c_k + b_h/\beta_h) > 0$, $(F_i + b_h/\beta_h) > 0$ ($k = 1, 2, \dots, r$;
 $i = 1, 2, \dots, u$; $h = 1, 2, \dots, m$).

then

$$(4.6) \quad w^\mu H_{p+r, q+s}^{m, n+r} \left[z^{\delta w \delta} \begin{matrix} \{(c_r, \delta)\}, \{(a_p, \delta a_p)\} \\ \{(b_q, \delta \beta_q)\}, \{(d_s, \delta)\} \end{matrix} \right] \times \\ = \frac{\Gamma(1 - c_r - \mu)}{\Gamma(1 - d_s - \mu)} \frac{\Gamma(F_u)}{\Gamma(f_t)} \sum_{N=0}^{\infty} \frac{(-1)^N}{N!} {}_{r+u+1}F_{s+t} \left[\begin{matrix} -N, 1 - c_r - \mu, F_u; w \\ f_t, 1 - d_s - \mu \end{matrix} \right] \times \\ \times H_{p+t+1, q+u+1}^{m, n+t+1} \left[z^{\delta} \begin{matrix} (-\mu, \delta), \{(1 - f_t - \mu, \delta)\}, \{(a_p, \delta a_p)\} \\ \{(b_q, \delta \beta_q)\}, \{(1 - F_u - \mu, \delta)\}, (N - \mu, \delta) \end{matrix} \right]$$

Proof: Firstly, we prove (4.6) for the case $u = 0, t = 1$ and $f_1 = a$, that is

$$(4.7) \quad w^\mu H_{p+r, q+s}^{m, n+r} \left[z^{\delta w \delta} \begin{matrix} \{(c_r, \delta)\}, \{(a_p, \delta a_p)\} \\ \{(b_q, \delta \beta_q)\}, \{(d_s, \delta)\} \end{matrix} \right] \\ = \frac{\Gamma(1 - c_r - \mu)}{\Gamma(\alpha)} \frac{\Gamma(1 - d_s - \mu)}{\Gamma(1 - \alpha)} \sum_{N=0}^{\infty} \frac{(-1)^N}{N!} {}_{r+1}F_{s+1} \left[\begin{matrix} -N, 1 - c_r - \mu; w \\ a, 1 - d_s - \mu \end{matrix} \right] \times \\ \times H_{p+2, q+1}^{m, n+2} \left[z^{\delta} \begin{matrix} (-\mu, \delta), (1 - \alpha - \mu, \delta), \{(a_p, \delta a_p)\} \\ \{(b_q, \delta \beta_q)\}, (N - \mu, \delta) \end{matrix} \right]$$

Our proof for (4.7) is based upon the induction on the parameters r and s .
(Note that the case $r = s = 0$ is the result (4.1) with $\alpha+1$ replaced by α). Now
to prove the induction on r , multiplying both the sides of (4.7) by $w^{-r-\mu} e^{-\lambda w}$
integrating w.r.t. w from 0 to ∞ , changing the order of summation and integration
on the right hand side and evaluating the integrals

$$\int_0^\infty w^{-\sigma} e^{-\lambda w} H_{p+r, q+s}^{m, n+r} \left[z^{\delta w \delta} \begin{matrix} \{(c_r, \delta)\}, \{(a_p, \delta a_p)\} \\ \{(b_q, \delta \beta_q)\}, \{(d_s, \delta)\} \end{matrix} \right] dw$$

and

$$\int_0^\infty w^{-\sigma-\mu} e^{-\lambda w} {}_{r+1}F_{s+1} \left[\begin{matrix} -N, 1 - c_r - \mu; w \\ a, 1 - d_s - \mu \end{matrix} \right] dw$$

with the help of (3.2) and [2, p. 219(17)], we get

$$\lambda^{-\mu} H_{p+r+1, q+s}^{m, n+r+1} \left[\frac{z^{\delta}}{\lambda^{\delta}} \begin{matrix} \{(c_r, \delta)\}, (\sigma, \delta), \{(a_p, \delta a_p)\} \\ \{(b_q, \delta \beta_q)\}, \{(d_s, \delta)\} \end{matrix} \right]$$

$$= \frac{\Gamma(1 - c_r - \mu)}{\Gamma(\alpha) \Gamma(1 - d_s - \mu)} \sum_{N=0}^{\infty} \frac{(-1)^N}{N!} {}_{r+2}F_{s+1} \left[\begin{matrix} -N, 1 - c_r - \mu, 1 - \sigma - \mu; \frac{1}{\lambda} \\ \alpha, 1 - d_s - \mu \end{matrix} \right] \times$$

$$\times H_{p+2, q+1}^{m, n+2} \left[z^\delta \middle| \begin{matrix} (-\mu, \delta), (1 - \alpha - \mu, \delta), \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\}, (N - \mu, \delta) \end{matrix} \right]$$

now replacing $1/\lambda$ by w and identifying σ with c_{r+1} , the induction on r is completed.

To perform the induction on s , multiplying both the sides of (4.7) by $w^{1-\mu-\sigma}$, replacing w by $1/\lambda$ and taking inverse Laplace transforms of

$$\lambda^{\sigma-1} H_{p+r, q+s}^{m, n+r} \left[\frac{z^\delta}{\lambda^\delta} \middle| \begin{matrix} \{(c_r, \delta)\}, \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\}, \{(d_s, \delta)\} \end{matrix} \right]$$

and

$$\lambda^{\sigma-1+\mu} {}_{r+1}F_{s+1} \left[\begin{matrix} -N, 1 - c_r - \mu; 1/\lambda \\ \alpha, 1 - d_s - \mu \end{matrix} \right]$$

by using (3.3) and [2, p. 297(1)], we obtain

$$w^\mu H_{p+r, q+s+1}^{m, n+r} \left[z^{\delta w^\delta} \middle| \begin{matrix} \{(c_r, \delta)\}, \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\}, \{(d_s, \delta)\}, (\sigma, \delta) \end{matrix} \right]$$

$$= \frac{\Gamma(1 - c_r - \mu)}{\Gamma(\alpha) \Gamma(1 - d_s - \mu) \Gamma(1 - \sigma - \mu)} \sum_{N=0}^{\infty} \frac{(-1)^N}{N!} {}_{r+1}F_{s+2} \left[\begin{matrix} -N, 1 - c_r - \mu; w \\ \alpha, 1 - d_s - \mu, 1 - \sigma - \mu \end{matrix} \right] \times$$

$$\times H_{p+2, q+1}^{m, n+2} \left[z^\delta \middle| \begin{matrix} (-\mu, \delta), (1 - \alpha - \mu, \delta), \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\}, (N - \mu, \delta) \end{matrix} \right],$$

identifying σ with d_{s+1} , the induction on s is completed.

Now to effect the induction of t multiplying both the sides of (4.6) by $z^{\sigma+\mu-1} e^{-\lambda z}$, integrating with respect to z from 0 to ∞ , interchanging the order of integration and summation on the right hand side, evaluating the integrals

$$\int_0^\infty z^{\sigma+\mu-1} e^{-\lambda z} H_{p+r, q+s}^{m, n+r} \left[z^\delta w^\delta \middle| \begin{matrix} \{(c_r, \delta)\}, \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\}, \{(d_s, \delta)\} \end{matrix} \right] dz$$

and

$$\int_0^\infty z^{\sigma+\mu-1} e^{-\lambda z} H_{p+t+1, q+u+1}^{m, n+t+1} \left[z^\delta \middle| \begin{matrix} (-\mu, \delta), \{(1 - f_t - \mu, \delta)\}, \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\}, \{(1 - F_u - \mu, \delta)\}, (N - \mu, \delta) \end{matrix} \right] dz$$

with the help of (3.2) and replacing λ by $1/z$ we get

$$(4.8) \quad w^\mu H_{p+r+1, q+s}^{m, n+r+1} \left[z^{\delta w^\delta} \middle| \begin{matrix} (1 - \sigma - \mu, \delta), \{(c_r, \delta)\}, \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\}, \{(d_s, \delta)\} \end{matrix} \right]$$

$$= \frac{\Gamma(1 - c_r - \mu)}{\Gamma(1 - d_s - \mu) \Gamma(f_t)} \sum_{N=0}^{\infty} \frac{(-1)^N}{N!} {}_{r+u+1}F_{s+t} \left[\begin{matrix} -N, 1 - c_r - \mu, F_u; w \\ f_t, 1 - d_s - \mu \end{matrix} \right] \times$$

$$\times H_{p+t+2, q+u+1}^{m, n+t+2} \left[z^\delta \middle| \begin{matrix} (-\mu, \delta), (1 - \sigma - \mu, \delta), \{(1 - f_t - \mu, \delta)\}, \{(a_p, \delta \alpha_p)\} \\ \{(b_q, \delta \beta_q)\}, \{(1 - F_u - \mu, \delta)\}, (N - \mu, \delta) \end{matrix} \right]$$

multiplying both the sides of (4.8) by w^σ , replacing w by $1/\lambda$ and taking the inverse Laplace transforms of

$$\lambda^{-\sigma-\mu} H_{p+r+1, q+s}^{m, n+r+1} \left[z^\delta \middle| \begin{array}{l} (1-\sigma-\mu, \delta), \{(c_r, \delta)\}, \{(a_p, \delta\alpha_p)\} \\ \{(b_q, \delta\beta_q)\}, \{(d_s, \delta)\} \end{array} \right]$$

and

$$\lambda^{-\sigma} F_{s+t}^{r+u+1} \left[\begin{array}{l} -N, 1-c_r-\mu, F_u; 1/\lambda \\ f_t, 1-d_s-\mu \end{array} \right]$$

with the help of (3.3) and [2, p. 297(1)], we obtain

$$\begin{aligned} & w^\mu H_{p+r, q+s}^{m, n+r} \left[z^\delta w^\delta \middle| \begin{array}{l} \{(c_r, \delta)\}, \{(a_p, \delta\alpha_p)\} \\ \{(b_q, \delta\beta_q)\}, \{(d_s, \delta)\} \end{array} \right] \\ &= \frac{\Gamma(1-c_r-\mu)}{\Gamma(1-d_s-\mu)} \frac{\Gamma(F_u)}{\Gamma(f_t) \Gamma(\sigma)} \sum_{N=0}^{\infty} \frac{(-1)^N}{N!} F_{s+t+1} \left[\begin{array}{l} -N, 1-c_r-\mu, F_u; w \\ f_t, 1-d_s-\mu \end{array} \right] \times \\ & \times H_{p+t+2, q+u+1}^{m, n+t+2} \left[z^\delta \middle| \begin{array}{l} (-\mu, \delta), (1-\sigma-\mu, \delta), \{(1-f_t-\mu, \delta)\}, \{(a_p, \delta\alpha_p)\} \\ \{(b_q, \delta\beta_q)\}, \{(1-F_u-\mu, \delta)\}, (N-\mu, \delta) \end{array} \right] \end{aligned}$$

identifying σ with f_{t+1} , the induction on t is completed.

To prove the induction on u , multiplying both the sides of (4.6) by $z^{p+\mu}$ replacing z by $1/\lambda$, and evaluating the inverse Laplace transforms of

$$\lambda^{-p-\mu} H_{p+r, q+s}^{m, n+r} \left[\frac{w^\delta}{\lambda^\delta} \middle| \begin{array}{l} \{(c_r, \delta)\}, \{(a_p, \delta\alpha_p)\} \\ \{(b_q, \delta\beta_q)\}, \{(d_s, \delta)\} \end{array} \right]$$

and

$$\lambda^{-p-\mu} H_{p+t+1, q+u+1}^{m, n+t+1} \left[\frac{1}{\lambda^\delta} \middle| \begin{array}{l} (-\mu, \delta), \{(1-f_t-\mu, \delta)\}, \{(a_p, \delta\alpha_p)\} \\ \{(b_q, \delta\beta_q)\}, \{(1-F_u-\mu, \delta)\}, (N-\mu, \delta) \end{array} \right]$$

with the help of (3.3), we have

$$\begin{aligned} (4.9) \quad & w^\mu H_{p+r, q+s+1}^{m, n+r} \left[z^\delta w^\delta \middle| \begin{array}{l} \{(c_r, \delta)\}, \{(a_p, \delta\alpha_p)\} \\ \{(b_q, \delta\beta_q)\}, \{(d_s, \delta)\}, (1-p-\mu, \delta) \end{array} \right] \\ &= \frac{\Gamma(1-c_r-\mu)}{\Gamma(1-d_s-\mu)} \frac{\Gamma(F_u)}{\Gamma(f_t)} \sum_{N=0}^{\infty} \frac{(-1)^N}{N!} F_{s+t} \left[\begin{array}{l} -N, 1-c_r-\mu, F_u; w \\ f_t, 1-d_s-\mu \end{array} \right] \times \\ & \times H_{p+t+1, q+u+2}^{m, n+t+1} \left[z^\delta \middle| \begin{array}{l} (-\mu, \delta), \{(1-f_t-\mu, \delta)\}, \{(a_p, \delta\alpha_p)\} \\ \{(b_q, \delta\beta_q)\}, \{(1-F_u-\mu, \delta)\}, (1-p-\mu, \delta), (N-\mu, \delta) \end{array} \right] \end{aligned}$$

Multiplying both the sides of (4.9) by $w^{p-1} e^{-\lambda w}$, integrating with respect to w from 0 to ∞ , interchanging the order of summation and integration on the right hand side and evaluating

$$\int_0^\infty w^{p+\mu-1} e^{-\lambda w} H_{p+r, q+s+1}^{m, n+r} \left[z^\delta w^\delta \middle| \begin{array}{l} \{(c_r, \delta)\}, \{(a_p, \delta\alpha_p)\} \\ \{(b_q, \delta\beta_q)\}, \{(d_s, \delta)\}, (1-p-\mu, \delta) \end{array} \right] du$$

and

$$\int_0^\infty w^{\rho-1} e^{-\lambda w} {}_{r+u+1}F_{s+t} \left[\begin{matrix} -N, 1-c_r-\mu, F_u; w \\ f_t, 1-d_s-\mu \end{matrix} \right] dw$$

with the help of (3·2) and [2, p. 219(17)], we obtain

$$\begin{aligned} & \frac{1}{\lambda^\mu} H_{p+r, q+s}^{m, n+r} \left[\begin{matrix} z^\delta \\ \lambda^\delta \end{matrix} \middle| \begin{matrix} \{(c_r, \delta)\}, \{(a_p, \delta\alpha_p)\} \\ \{(b_q, \delta\beta_q)\}, \{(d_s, \delta)\} \end{matrix} \right] \\ &= \frac{\Gamma(1-c_r-\mu) \Gamma(F_u) \Gamma(\rho)}{\Gamma(1-d_s-\mu) \Gamma(f_t)} \sum_{N=0}^{\infty} \frac{(-1)^N}{N!} {}_{r+u+2}F_{s+t} \left[\begin{matrix} -N, 1-c_r-\mu, F_u, \rho; 1/\lambda \\ f_t, 1-d_s-\mu \end{matrix} \right] \times \\ & \times H_{p+t+1, q+u+2}^{m, n+t+1} \left[\begin{matrix} (-\mu, \delta), \{(1-f_t-\mu, \delta)\}, \{(a_p, \delta\alpha_p)\} \\ \{(b_q, \delta\beta_q)\}, \{(1-F_u-\mu, \delta)\}, (1-\rho-\mu, \delta), (N-\mu, \delta) \end{matrix} \right] \end{aligned}$$

replacing $1/\lambda$ by w and identifying ρ with F_{u+1} , the induction on u is completed.

Inversion of the order of integration and summation, in the proof of the above expansion is in-accordance with [5, p. 500], under the conditions stated in the theorem.

By virtue of the identity (4·5), the right hand side of (4·6) can also be written in an alternative form.

Theorem II.

Assumptions :

(i) p, q, r, s, t, u, m and n are positive integers such that $1 \leq m+s \leq q+s$, $0 \leq m+t \leq q+t$, $0 \leq n \leq p+r$, $0 \leq n \leq p+u+1$ and δ is a positive number.

(ii) Let none of the quantities be negative integers

$$d_j + \mu - 1 \quad (j = 1, 2, \dots, s); \quad F_i - 1 \quad (i = 1, 2, \dots, u).$$

(iii) Let $\sum_1^q (\beta_j) - \sum_1^p (\alpha_j) + (s-r) > 0$ when $z^\delta w^\delta \neq 0$; $\sum_1^q (\beta_j) - \sum_1^p (\alpha_j) + (s-r) = 0$

when $0 < |z^\delta w^\delta| < \beta^{-1}$ where $\beta = \delta^{(p+r-q-s)\delta} \prod_{j=1}^p (\alpha_j)^{a_j} \prod_{j=1}^q (\beta_j)^{-\beta_j}$;

$\sum_1^q (\beta_j) - \sum_1^p (\alpha_j) + (t-u) > 0$ when $z^\delta \neq 0$; $\sum_1^q (\beta_j) - \sum_1^p (\alpha_j) + (t-u) = 0$

when $0 < |z^\delta| < \alpha^{-1}$ where $\alpha = \delta^{(p+u-q-t)\delta} \prod_{j=1}^p (\alpha_j)^{a_j} \prod_{j=1}^q (\beta_j)^{-\beta_j}$.

(iv) Let $\delta \left[\sum_1^m (\beta_j) - \sum_{m+1}^q (\beta_j) + \sum_1^n (\alpha_j) - \sum_{n+1}^p (\alpha_j) + (s-r) \right] \equiv \lambda > 0$, $|\arg z^\delta w^\delta| < \frac{1}{2}\lambda\pi$

and $\delta \left[\sum_{j=1}^m (\beta_j) - \sum_{m+1}^q (\beta_j) + \sum_{j=1}^n (\alpha_j) - \sum_{n+1}^p (\alpha_j) + (t-u) \right] \equiv \phi > 0$, $|\arg z^\delta| < \frac{1}{2}\phi\pi$.

- (v) Let $\alpha_i(b_h+v) \neq \beta_h(a_i-\eta-1)$; $\alpha_i(d_k+v) \neq (a_i-\eta-1)$,
 $\alpha_i(f_l-\mu+v) \neq (a_i-\eta-1)$; $\alpha_i(1-\mu+v) \neq (-a_i-\eta-1)$
 $(v, \eta=0, 1, \dots; h=1, 2, \dots, m; i=1, 2, \dots, n; k=1, 2, \dots, s, l=1, 2, \dots, t)$
- (vi) Let $s+u+1 = r+t$.

(vii) Let $\sum_{j=1}^s d_j - \sum_{j=1}^r c_j + \sum_{j=1}^u F_j - \sum_{j=1}^t f_j - 2(1-a_i)/\alpha_i < (s-r)\mu - \frac{1}{2}$,

$$[d_h+(1-a_i)/\alpha_i] > 0, [F_h+(1-a_i)/\alpha_i] > 0$$

$(k=1, 2, \dots, s; h=1, 2, \dots, u; i=1, 2, \dots, n)$,

then

$$(4.10) \quad w^\mu H_{p+r, q+s}^{m+s, n} \left[z^\delta w^\delta \begin{matrix} \{(a_p, \delta\alpha_p)\}, \{(c_r, \delta)\} \\ \{(d_s, \delta)\}, \{(b_q, \delta\beta_q)\} \end{matrix} \right]$$

$$= \frac{\Gamma(d_s+\mu)}{\Gamma(c_r+\mu)} \frac{\Gamma(F_u)}{\Gamma(f_t)} \sum_{N=0}^{\infty} \frac{(-1)^N}{N!} {}_{s+u+1}F_{r+t} \left[\begin{matrix} -N, d_s+\mu, F_u; 1/w \\ f_t, c_r+\mu \end{matrix} \right] \times$$

$$\times H_{p+u+1, q+t+1}^{m+t+1, n} \left[z^\delta \begin{matrix} \{(a_p, \delta\alpha_p)\}, \{(F_u-\mu, \delta)\}, (1-N-\mu, \delta) \\ (1-\mu, \delta), \{(f_t-\mu, \delta)\}, \{(b_q, \delta\beta_q)\} \end{matrix} \right],$$

The proof of theorem II follows on the similar lines as that of theorem I.

With the help of the identity

$$(4.11) \quad H_{p+1, q+1}^{m+1, n} \left[x \begin{matrix} \{(a_p, \alpha_p)\}, (1-N-\mu, \delta) \\ (1-\mu, \delta), \{(b_q, \beta_q)\} \end{matrix} \right]$$

$$= (-1)^N H_{p+1, q+1}^{m, n+1} \left[x \begin{matrix} (1-N-\mu, \delta), \{(a_p, \alpha_p)\} \\ \{(b_q, \beta_q)\}, (1-\mu, \delta) \end{matrix} \right]$$

which easily follows from the definition of H-function; the right hand side of (4.10) can also be written in an alternative form.

Note that the expansion formulae are valid under the assumptions stated in the theorems. Even when the expansions diverge, a meaning in the asymptotic sense can often be assigned to the series which make the theorems useful both theoretically and computationally.

5. Particular cases

- (i) In (4.6), taking $\mu = 0, t = u = 0, s = r = l$, we get a result given by the author [1, (4.1)], with z and w replaced by w and λ .
- (ii) In (4.10), putting $\mu = 0, t = u = 0, s = r = l$, replacing z and w by w and λ , we get a result due to author [1, (4.4)].

- (iii) With $\mu = 0$, $\delta = 1$, $\alpha_j = \beta_h = 1$ ($j = 1, 2, \dots, p$; $h = 1, 2, \dots, q$), f_t and F_u respectively replaced by α_t and β_u ; (4.6) in view of (2.6), reduces to a known result [12, p. 360(2.3)].
- (iv) In (4.10), setting $\mu = 0$, $\delta = 1$, $\alpha_j = \beta_h = 1$ ($j = 1, 2, \dots, p$; $h = 1, 2, \dots, q$), replacing f_t and F_u respectively by α_t and β_u , using (4.11) and (2.6) we get a known relation [12, p. 362(2.7)].
- (v) Using (2.7), the results (4.6) and (4.10) reduce to expansions for Wright's generalized hypergeometric function.

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References

1. Anandani, P. Some expansion formulae for H-function—II. *Ganita*, **18**(2) : 89–101, 1967.
2. Bateman Project. Tables of integral transforms, Vol. I, McGraw-Hill, 1954.
3. Bateman Project. Tables of integral transforms Vol. II, McGraw-Hill, 1954.
4. Braaksma, B. L. J. Asymptotic expansions and analytic continuations for a class of Barnes-integrals. *Com. Math.* **15** : 239–341, 1963.
5. Bromwich, T. J. I. An introduction to the theory of infinite series, *Macmillan, New York*, 1955.
6. Fields, J. L. and Luke, Y. L. Asymptotic expansions of a class of hypergeometric polynomials with respect to the order I. *Jour. Math. Anal. App.*, **6** : 394–403, 1963.
7. Fields, J. L. and Luke, Y. L. *ibid.*, II. *Jour. Math. Anal. App.* **7** : 440–445, 1963.
8. Fox, C. The G.-and H-functions as symmetrical Fourier kernels. *Trans. Amer. Math. Soc.*, **3** : Vol. 98, 395–429, 1961.
9. Gupta, K. C. and Jain, U. C. The H-function—II. *To appear in Proc. Nat. Acad. Sci., India*.
10. Lebedev, N. N. Special functions and their applications. *Prentice-Hall Inc.*, 1965.
11. Rainville, E. D. Special functions, *Macmillan, New York*, 1960.
12. Wimp, J. and Luke, Y. L. Expansions formulas for generalized hypergeometric functions. *Rendi Conti Del. Circolo Mat di Palermo II*, 351–366, 1962.
13. Wright, E. M. The asymptotic expansions of generalized hypergeometric functions. *Jour. Lond. Math. Soc.*, **10** : 286–293, 1935.

Some Formulae involving Hermite, Laguerre and Gegenbauer Polynomials

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Abstract

In this paper an attempt is made to obtain some formulae, mostly generating functions, involving Hermite, Laguerre and Gegenbauer polynomials.

1. Introduction

This paper is in continuation of [4] and is aimed at obtaining new formulas involving Hermite, Laguerre and Gegenbauer polynomials by employing the conception of fractional derivatives defined by

$$(1) \quad D_w^\lambda \{ w^{\mu-1} \} = \frac{d^\lambda}{dw^\lambda} \{ w^{\mu-1} \} = \frac{\Gamma(\mu)}{\Gamma(\mu-\lambda)} w^{\mu-\lambda-1}.$$

Throughout we shall be applying the definition (1) on series of the type $\sum A(n) x^{\lambda+n-1}$ and $\sum A(n, k) x^{\lambda+n+k-1}$ and our object, as such, would be to augment parameters by differentiating these series term by term.

2. Let us consider the generating function

$$(2) \quad \sum_{n=0}^{\infty} \frac{(H_n(x))}{n!} t^n = e^{2xt-t^2}$$

Replacing t by $(1-y)t$, we obtain

$$\sum_{n=0}^{\infty} \frac{H_n(x)}{n!} t^n (1-y)^n e^{2t(x-t)y} = e^{2xt-t^2} e^{-t^2y^2}.$$

Multiplying both the sides by $y^{\lambda-1}$ and applying the operator $D_y^{\lambda-\mu}$, it becomes

$$\begin{aligned} & \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} t^n D_y^{\lambda-\mu} \left\{ \sum_{r=0}^n \sum_{k=0}^{\infty} \frac{(-n)_r}{r! k!} (2xt-t^2)^k y^{\lambda+r+k-1} \right\} \\ &= e^{2xt-t^2} D_y^{\lambda-\mu} \left\{ \sum_{n=0}^{\infty} \frac{(-t^2)^n}{n!} y^{\lambda+2n-1} \right\} \end{aligned}$$

Now

$$D_y^{\lambda-\mu} \left\{ \sum_{r=0}^n \sum_{k=0}^{\infty} \frac{(-n)_r}{r! k!} (2xt+2t^2)^k y^{\lambda+r+k-1} \right\}$$

$$= \frac{\Gamma(\lambda)}{\Gamma(\mu)} y^{\mu-1} \phi_1 [\lambda; -n; \mu; y, 2t(x-t)y]$$

and

$$D_y^{\lambda-\mu} \left\{ \sum_{n=0}^{\infty} \frac{(-t^2)^n}{n!} y^{\lambda+2n-1} \right\} = \frac{\Gamma(\lambda)}{\Gamma(\mu)} y^{\mu-1} {}_2F_2 (\tfrac{1}{2}\lambda, \tfrac{1}{2}\lambda + \tfrac{1}{2}; \tfrac{1}{2}\mu, \tfrac{1}{2}\mu + \tfrac{1}{2}; -t^2 y^2).$$

Thus we arrive at

$$(3) \quad \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} \phi_1 [\lambda; -n; \mu; y, 2t(x-t)y] t^n = e^{2xt-t^2} {}_2F_2 (\tfrac{1}{2}\lambda, \tfrac{1}{2}\lambda + \tfrac{1}{2}; \tfrac{1}{2}\mu, \tfrac{1}{2}\mu + \tfrac{1}{2}; -t^2 y^2).$$

For the definition of ϕ_1 see [2, p. 225].

If we put $y = 1$ and $\lambda = -m$, (3) becomes

$$(4) \quad \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} L_m^{(\mu+n)}(2xt-2t^2) = \frac{(1+\mu)_m}{m!} e^{2xt-t^2} F[-\tfrac{1}{2}m, -\tfrac{1}{2}m + \tfrac{1}{2}; \tfrac{1}{2}\mu + \tfrac{1}{2}, \tfrac{1}{2}\mu + 1; -t^2].$$

Again, putting $x = t$, dividing y by λ and letting $\lambda \rightarrow \infty$, it follows from (3) that

$$(5) \quad \sum_{n=0}^{\infty} \frac{t^n}{(1+\mu)_n} H_n(t) L_n^{(\mu)}(y) = e^{t^2} {}_0F_2 (-; \tfrac{1}{2}\mu + \tfrac{1}{2}, \tfrac{1}{2}\mu + 1; -\tfrac{1}{4}t^2 y^2).$$

We rewrite the generating function (2) as

$$\sum_{n=0}^{\infty} \frac{H_n(x)}{n!} t^n e^{-2xt} = e^{-t^2}$$

Multiplying both the sides by $t^{\lambda-1}$ and applying the operator $D_t^{\lambda-\mu-1}$, it becomes

$$\sum_{n=0}^{\infty} \frac{H_n(x)}{n!} D_t^{\lambda-\mu-1} \left\{ \sum_{r=0}^{\infty} \frac{(-2x)^r}{r!} t^{\lambda+n+r-1} \right\} = D_t^{\lambda-\mu-1} \left\{ \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} t^{\lambda+2n-1} \right\}.$$

Since

$$D_t^{\lambda-\mu-1} \left\{ \sum_{r=0}^{\infty} \frac{(-2x)^r}{r!} t^{\lambda+n+r-1} \right\} = \frac{\Gamma(\lambda+n)}{\Gamma(\mu+n+1)} t^{\mu+n} {}_1F_1 (\lambda+n; \mu+n+1; -2xt)$$

and

$$D_t^{\lambda-\mu-1} \left\{ \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} t^{\lambda+2n-1} \right\} = \frac{\Gamma(\lambda)}{\Gamma(\mu+1)} t^{\mu} {}_2F_2 (\tfrac{1}{2}\lambda, \tfrac{1}{2}\lambda + \tfrac{1}{2}; \tfrac{1}{2}\mu + \tfrac{1}{2}, \tfrac{1}{2}\mu + 1; -t^2),$$

it follows that

$$(6) \quad \sum_{n=0}^{\infty} \frac{(\lambda)_n}{(\mu+1)_n} \frac{H_n(x)}{n!} {}_1F_1 (\lambda+n; \mu+n+1; -2xt) t^n = {}_2F_2 (\tfrac{1}{2}\lambda, \tfrac{1}{2}\lambda + \tfrac{1}{2}; \tfrac{1}{2}\mu + \tfrac{1}{2}, \tfrac{1}{2}\mu + 1; -t^2).$$

In case $\lambda = \mu + m + 1$, (6) yields the known result due to Salam [1].

Similarly, if we write down (2) in the form

$$\sum_{n=0}^{\infty} \frac{H_n(x)}{n!} t^{\lambda+n-1} e^{t^2} = t^{\lambda-1} e^{2xt}$$

and employ the operator $D_t^{\lambda-\mu-1}$, we obtain

$$\sum_{n=0}^{\infty} \frac{(\lambda)_n}{(\mu+1)_n} \frac{H_n(x)}{n!} {}_2F_2 \left[\begin{matrix} \frac{1}{2}(\lambda+n), \frac{1}{2}(\lambda+n+1); \\ \frac{1}{2}(\mu+n+1), \frac{1}{2}(\mu+n+2) \end{matrix} t^2 \right] t^n = {}_1F_1 (\lambda; \mu+1; 2xt).$$

3. Now we consider the generating function for Laguerre polynomial

$$(8) \quad \sum_{n=0}^{\infty} \frac{L_n^{(\alpha)}(x)}{(1+\alpha)_n} t^n e^{-t} = {}_1F_1 (-; 1+\alpha; -xt)$$

Multiplying both the sides by $t^{\lambda-1}$ and applying the operator $D_t^{\lambda-\mu-1}$ we get

$$\sum_{n=0}^{\infty} \frac{L_n^{(\alpha)}(x)}{(1+\alpha)_n} D_t^{\lambda-\mu-1} \left\{ \sum_{r=0}^{\infty} \frac{(-1)^r}{r!} t^{\lambda+n+r-1} \right\} = D_t^{\lambda-\mu-1} \left\{ \sum_{n=0}^{\infty} \frac{(-x)^n}{n! (1+\alpha)_n} t^{\lambda+n-1} \right\},$$

which yields

$$(9) \quad \sum_{n=0}^{\infty} \frac{(\lambda)_n}{(1+\alpha)_n (1+\mu)_n} L_n^{(\alpha)}(x) {}_1F_1 (\mu-\lambda+1; \mu+n+1; t) t^n = e^t {}_1F_2 (\lambda; 1+\alpha, 1+\mu; -xt).$$

For $\lambda = \mu + m + 1$, (8) reduces to the formula due to Halim and Salam [3].

4. Lastly, we take up the generating function

$$(10) \quad \sum_{n=0}^{\infty} C_n^{(\alpha)}(x) t^n = (1 - 2xt + t^2)^{-\alpha} = (x + \sqrt{x^2-1} - t)^{-\alpha} (x - \sqrt{x^2-1} - t)^{-\alpha}.$$

We replace t by $(1-y)t$, multiply both the sides by $y^{\beta-1}$ and apply the operator $D_y^{\beta-\gamma}$, so that

$$\begin{aligned} & \sum_{n=0}^{\infty} C_n^{(\alpha)}(x) t^n D_y^{\beta-\gamma} \left\{ \sum_{r=0}^n \frac{(-n)_r}{r!} y^{\beta+r-1} \right\} \\ &= y^{-2\alpha} D_y^{\beta-\gamma} \left\{ \sum_{n,r=0}^{\infty} \frac{(\alpha)_n (\alpha)_r}{n! r!} \left(\frac{-t}{x + \sqrt{x^2-1}-t} \right)^n \left(\frac{-t}{x - \sqrt{x^2-1}-t} \right)^r y^{\beta+n+r-1} \right\} \end{aligned}$$

where $= (1 - 2xt + t^2)^{\frac{1}{2}}$.

Now

$$D_y^{\beta-\gamma} \left\{ \sum_{r=0}^n \frac{(-n)_r}{r!} y^{\beta+r-1} \right\} = \frac{\Gamma(\beta)}{\Gamma(\gamma)} y^{\gamma-1} {}_2F_1 (-n, \beta; \gamma; y)$$

$$\begin{aligned} \text{and } & D_y^{\beta-\gamma} \left\{ \sum_{n,r=0}^{\infty} \frac{(\alpha)_n (\alpha)_r}{n! r!} \left(\frac{-t}{x + \sqrt{x^2-1}-t} \right)^n \left(\frac{-1}{x - \sqrt{x^2-1}-1} \right)^r y^{\beta+n+r-1} \right\} \\ &= \frac{\Gamma(\beta)}{\Gamma(\gamma)} y^{\gamma-1} {}_2F_1 (\beta; \alpha, \alpha; \gamma; \frac{-yt}{x + \sqrt{x^2-1}-t}, \frac{-yt}{x - \sqrt{x^2-1}-t}). \end{aligned}$$

Therefore it follows that

$$(11) \quad \sum_{n=0}^{\infty} C_n^{(\alpha)}(x) {}_2F_1(-n, \beta; \gamma, y) t^n = \rho^{-2\alpha} F_1(\beta; \alpha, \alpha; \gamma; \frac{-yt}{x + \sqrt{x^2-1-t}}, \frac{-yt}{x - \sqrt{x^2-1-t}}),$$

If we divide y by β and let $\beta \rightarrow \infty$, (11) yields.

$$(12) \quad \sum_{n=0}^{\infty} \frac{n!}{(\gamma)_n} C_n^{(\alpha)}(x) L_n^{(\gamma-1)}(y) t^n = \rho^{-2\alpha} \phi_2 \left(\alpha, \alpha; \gamma; \frac{-yt}{x + \sqrt{x^2-1-t}}, \frac{-yt}{x - \sqrt{x^2-1-t}} \right)$$

For the definition of ϕ_2 see [2, p. 225].

Further, if we put $\gamma = 2\alpha$ and then use the relation

$$\phi_2(\alpha, \alpha; 2\alpha; 2x, 2y) = e^{x+y} {}_0F_1[-; \alpha + \frac{1}{2}; \frac{1}{4}(x-y)^2],$$

(12) reduces to

$$(13) \quad \sum_{n=0}^{\infty} \frac{n!}{(2\alpha)_n} C_n^{(\alpha)}(x) L_n^{(2\alpha-1)}(y) t^n = \rho^{-2\alpha} e^{-\frac{yt}{\rho^2}(x-t)} x {}_0F_1 \left[-; \frac{y^2 t^2 (x^2-1)}{4\rho^4} \right].$$

(13) is due to Weisner [5].

References

- [1] Al Salam, W. A. Operational representation for the Laguerre and other polynomials. *Duke Maths. J.*, **31**, 127-142, 1964.
- [2] Erdelyi, A. Higher Transcendental Functions, Vol. I : 1953.
- [3] Halim, N. A. and Al-Salam, W. A. Double Euler Transformation of certain hypergeometric functions. *Duke J. Maths.* **13**, 51-62, 1963.
- [4] Manocha, H. L. and Sharma, B. L. Infinite Series of Hypergeometric Functions. *Annales de la Societe de Bruxelles*, **T. 80**, 1, 73-86, 1966.
- [5] Weisner, L. Group theoretic origins of certain generating functions. *Pacific J. Math.*, **5**, 1033-39, 1955.

Series solution of Dual integral equations with Bessel Function Kernels

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Abstract

In the analysis of mixed boundary value problems we encounter dual integral equations of the type

$$(1) \quad \int_0^\infty t^\alpha J_\mu(xt) g(t) dt = f(x), \quad 0 < x < 1$$

$$(2) \quad \int_0^\infty t^\beta J_\nu(xt) g(t) dt = F(x), \quad x > 1;$$

where $f(x)$, $F(x)$ are given functions of x and $g(t)$ is to be determined.

A solution of the dual integral equations (1) and (2) is given in the form :

$$(3) \quad g(t) = \sum_{m=n+1}^{\infty} a_m t^{\lambda-\alpha} J_{\mu+\lambda+2m+1}(t),$$

valid for $n = 0, 1, 2, \dots, R(\mu + 1) > 0, R(\lambda + 1) > 0, m \neq n,$

$$R(2\mu + \lambda + 2m + 2) > R(-\lambda) > -1,$$

$$R(\nu + \mu + \lambda + 2m + 2) > R(\alpha - \beta - \lambda) > -1.$$

A few particular cases have also been given.

1. Introduction

In the analysis of mixed boundary value problems, we encounter dual integral equations of the type

$$(1) \quad \int_0^\infty t^\alpha J_\mu(xt) g(t) dt = f(x), \quad 0 < x < 1$$

$$(2) \quad \int_0^\infty t^\beta J_\nu(xt) g(t) dt = F(x), \quad x > 1;$$

where $f(x)$, $F(x)$ are given functions of x and $g(t)$ is to be found.

Tranter⁴ solved the pair of integral equation (1) and (2) for the case when $\mu = \nu = 0$, $\beta = 0$, $F(x) \equiv 0$, and applied his solution to potential problems with axial symmetry.

In a different paper, Tranter⁵ derived the solution of the dual integral equations (1) and (2) for the case in which $\mu = \nu$, $\beta = 0$, $F(x) \equiv 0$ and utilized the method in solving the diffraction problem of electromagnetic waves.

Recently, Sneddon² has given a formal solution of the dual integral equations with trigonometrical kernels. Sneddon's results have been generalized by Srivastava³ by taking Bessel function and trigonometrical kernels in the dual integral equations.

The object of the present note is to generalise further the results of Srivastava by using the following result due to Tranter [6, p. 97].

$$(3) \quad \int_0^{\pi/2} J_\mu(z \sin \theta) {}_2F_1(-n, \mu + \nu + n + 1; \mu + 1; \sin^2 \theta) \sin^{\mu+1} \theta \cos^{\nu+1} \theta d\theta \\ = 2^\nu z^{-\nu-1} \Gamma(\mu + 1) \Gamma(\nu + n + 1) [\Gamma(\mu + n + 1)]^{-1} J_{\mu+\nu+2n+1}(z),$$

valid for $n = 0, 1, 2, \dots$, $R(\mu + 1) > 0$, $R(\nu + 1) > 0$.

2. Solution of (1) and (2).

Given that the functions $f(x)$ and $F(x)$ can be represented in series of Gauss's hypergeometric functions in the forms

$$(4) \quad f(x) = \sum_{m=1}^{\infty} a_m 2^\lambda x^\mu \Gamma(\mu + \lambda + m + 1) [\Gamma(\mu + 1) \Gamma(m + 1)]^{-1} {}_2F_1(\mu + \lambda + m + 1, -m; \mu + 1; x^2),$$

$$(5) \quad F(x) = \sum_{m=1}^{\infty} 2^{\lambda+\beta-\alpha} x^{-2\lambda-2m-2-\mu-\beta+\alpha} a_m \Gamma((\lambda+m+1 + \mu/2 + \nu/2 + \beta/2 - \alpha/2) \\ [\Gamma(\mu + \lambda + 2m + 2) \Gamma(-\lambda - m - \beta/2 + \alpha/2 + \nu/2 - \mu/2)]^{-1}$$

$${}_2F_1[\lambda+m+1+(\mu+\nu-\alpha+\beta)/2, \lambda+m+1+(\mu-\nu-\alpha+\beta)/2; \mu+\lambda+2m+2; 1/x^2],$$

and $f(x)$ satisfies the condition

$$(6) \quad \int_0^1 x^{\mu+1} (1-x^2)^\lambda {}_2F_1(-n, \mu + \nu + n + 1; \mu + 1; x^2) f(x) dx = 0;$$

then the solution to the dual integral equations is

$$(7) \quad g(t) = \sum_{m=n+1}^{\infty} a_m t^{\lambda-\alpha} J_{\mu+\lambda+2m+1}(t),$$

valid for $n = 0, 1, 2, \dots$, $R(\mu + 1) > 0$, $R(\lambda + 1) > 0$, $m \neq n$,

$$R(2\mu + \lambda + 2m + 2) > R(-\lambda) > -1, R(\nu + \mu + \lambda + 2 + 2m) > R(\alpha - \beta - \lambda) > -1.$$

3. Verification

On substituting the expression for $f(x)$ from (1), interchanging the order of integration and evaluating the x -integral by (3), we have

$$\int_0^1 x^{\mu+1} (1-x^2)^\lambda {}_2F_1(-n, \mu + \nu + n + 1; \mu + 1; x^2) f(x) dx$$

$$\begin{aligned}
&= 2^\lambda \Gamma(\mu + 1) \Gamma(\lambda + n + 1) [\Gamma(\mu + n + 1)]^{-1} \\
&\times \int_0^\infty t^{\alpha-\lambda-1} J_{\mu+\lambda+2n+1}(t) g(t) dt \\
&= 0, \text{ when } m \neq n.
\end{aligned}$$

The right hand side of the above expression becomes zero when we make use of (7), interchange the order of integration and summation and evaluate the t -integral by [7, p. 404].

(4) and (5) are easily obtainable from [1, p. 48 (9)].

The solution of the integral equations (1) and (2) for the case in which $n = 0$, $\alpha = 2k - 3/2$, $\beta = 1/2$, $\mu = \nu$, $\lambda = k - 1$, $F(x) \equiv 0$ is a known result due to Srivastava³.

References

1. Erdelyi, A. et al. Tables of integral transforms, Vol. II, McGraw-Hill, New York, 1954.
2. Sneddon, I. N. Dual integral equations with trigonometrical kernels, *Proc. Glasgow Math. Association*, **5**, 147-152, 1962.
3. Srivastava, K. N. Dual integral equations with Bessel function and trigonometrical kernels. *Proc. Edin. Math. Soc.*, **13**, 351-354, 1963.
4. Tranter, G. J. On some dual integral equations occurring in potential problems with axial symmetry. *Quart. J. Mech. and Applied Math.*, **3**, 411-419, 1950.
5. Tranter, C. J. A further note on dual integral equations and an application to the diffraction of electromagnetic waves. *Quart. J. Mech. and Applied Math.*, **7**, 317-325, 1954.
6. Tranter, C. J. A generalization of Sonine's first finite integral. *Proc. Glasgow Math. Association*, **6**, 97-98, 1963.
7. Watson, G. N. A treatise on the theory of Bessel functions. Cambridge University Press, 1944.

On a generalised Stieltjes transform

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Abstract

In this paper we obtain the image of the H-function defined by Fox in the generalised Stieltjes transform. Later on certain recurrence relations for the H-function are established. Since this is a very general function many results can be derived by giving particular values to the parameters.

1. Introduction

The aim of this paper is to obtain some recurrence relations for the H-function defined by Fox [4, Page 408]. The method used is that of operational calculus. First we give images of the H-function in the following transform

$$(1) \quad f(s) = s^{-1} \int_0^\infty {}_2F_1(a, b; c; -t/s) \theta(t) dt$$

where $c \neq 0, -1, -2, -3, \dots$. Transform (1) is a generalisation of Stieltjes transform

$$(2) \quad f(s) = \int_0^\infty (s+t)^{-1} \theta(t) dt.$$

For (1) reduces to (2) when $a = c$ and $b = 1$.

Later on the image of the H-function thus obtained are used to establish the recurrence relations.

Since Meijer's G-fuction [1, page 207] is a special case of the H-function, the image of the G-function in the transforms (1) and (2) and the recurrence relations for the G-function follow as particular cases of our results.

The definition of the H-function used here has slight difference in the parameters to that given by Fox. We define

$$(3) \quad H_{p, q}^{m, n} \left[x \mid \begin{matrix} (a_1, e_1), (a_2, e_2), \dots, (a_p, e_p) \\ (b_1, f_1), (b_2, f_2), \dots, (b_q, f_q) \end{matrix} \right]$$

$$= \frac{1}{2\pi i} \int_L \frac{\prod_{j=1}^m \Gamma(b_j - f_j \xi)}{\prod_{j=m+1}^q \Gamma(1 - b_j + f_j \xi)} \frac{\prod_{j=1}^n (1 - a_j + e_j \xi)}{\prod_{j=n+1}^p \Gamma(a_j - e_j \xi)} x^\xi d\xi;$$

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where an empty product is interpreted as unity, $0 \leq m \leq q$, $0 \leq n \leq p$; e^s 's and f^s 's are all positive. L is a suitable contour of Barnes type such that the poles of $\Gamma(b_j - f_j \xi)$, $j = 1, 2, 3, \dots, m$ lie on the right hand side of the contour and those of $\Gamma(1 - a_j + e_j \xi)$, $j = 1, 2, \dots, n$ lie on the left hand side. Also the parameters are so restricted that the integral on the right hand side of (3) is convergent.

If we apply the formula :

$$\Gamma(mz) = (2\pi)^{\frac{1}{2}-\frac{1}{m}} \cdot m^{mz-\frac{1}{2}} \cdot \prod_{j=0}^{m-1} \Gamma\left(z + \frac{j}{m}\right)$$

to the right hand side of (3) we arrive at the following simple but interesting formula connecting the H-function and the G-function

$$(4) \quad H_{p, q}^{m, n} \left[\begin{matrix} (a_1, s), (a_2, s), \dots, (a_p, s) \\ (b_1, s), (b_2, s), \dots, (b_q, s) \end{matrix} \right] = s^{-1} G_{p, q}^{m, n} \left(\begin{matrix} a_1, a_2, \dots, a_p \\ b_1, b_2, \dots, b_q \end{matrix} \right)$$

where s is a positive integer.

In this paper we have assumed all parameters to be real.

2. The following result will be proved in this section :

$$(5) \quad s^{-1} \int_0^\infty {}_2F_1(a, b; c; -t/s) \phi(t) dt = \frac{\Gamma(c)}{\Gamma(a) \Gamma(b)} \cdot t^l \times \\ \times H_{p+2, q+2}^{m+2, n+1} \left[\begin{matrix} (-l, \sigma), (a_1, e_1), \dots, (a_p, e_p), (c-l-1, \sigma) \\ (a-l-1, \sigma), (b-l-1, \sigma), (b_1, f_1), \dots, (b_q, f_q) \end{matrix} \right]$$

where

$$\phi(t) = t^l H_{p, q}^{m, n} \left[\begin{matrix} (a_1, e_1), (a_2, e_2), \dots, (a_p, e_p) \\ (b_1, f_1), (b_2, f_2), \dots, (b_q, f_q) \end{matrix} \right]$$

provided that $(\sigma) > 0$, $(s) > 0$, $\left(1 + l + \sigma \frac{b_h}{f_h}\right) > 0$, $\left(b - l - 1 - \sigma \frac{b_h}{f_h}\right) > 0$

and $\left(a - l - 1 - \sigma \frac{b_h}{f_h}\right) > 0$, ($h = 0, 1, 2, \dots, m$) and one of the following sets of

conditions are satisfied :

- (i) $\lambda > 0$, $|\arg(z)| < \frac{1}{2}\pi\lambda$,
- (ii) $\lambda \geq 0$, $|\arg(z)| \leq \frac{1}{2}\pi\lambda$, $(\mu + 1) > 0$, $(\mu + l + 1) < 0$.

Here λ and μ stand for the quantities

$$\sum_{j=1}^n (e_j) - \sum_{j=n+1}^p (e_j) + \sum_{j=1}^m (f_j) - \sum_{j=m+1}^q (f_j)$$

and

$$\frac{1}{2}(p - q) + \sum_{j=1}^q (b_j) - \sum_{j=1}^p (a_j)$$

respectively.

If we put $a = c$ and $b = 1$ in (5) we get the following image of the H-function in the well known Stieltjes transform

$$(6) \quad \int_0^\infty (s+t)^{-1} \theta(t) dt \\ = s^l H_{p+1, q+1}^{m+n+1} \left[z s^\sigma \begin{array}{|c} \hline (-l, \sigma), (a_1, e_1), \dots, (a_p, e_p) \\ \hline (-l, \sigma), (b_1, f_1), \dots, (b_q, f_q) \\ \hline \end{array} \right]$$

where $(\sigma) > 0$, $(s) > 0$, $0 > \left(l + \sigma \frac{b_h}{f_h} \right) > -1$, ($h = 0, 1, 2, \dots, m$) the other conditions of validity being one of the conditions (i), (ii) of (5).

The following result will be used in the proof of (5) [1, page 79]

$$(7) \quad \frac{\Gamma(a+s)\Gamma(b+s)\Gamma(c)\Gamma(-s)}{\Gamma(a)\Gamma(b)\Gamma(c+s)} = \int_0^\infty {}_2F_1(a, b; c; -z) \cdot Z^{-s-1} dz.$$

Proof of (5) : From (1)

$$(8) \quad \begin{aligned} & s^{-1} \int_0^\infty {}_2F_1(a, b; c; -t/s) \phi(t) dt \\ &= s^{-1} \int_0^\infty t^l {}_2F_1(a, b; c; -t/s) \times \\ & \times H_{p, q}^{m, n} \left[z t^\sigma \begin{array}{|c} \hline (a_1, e_1), (a_2, e_2), \dots, (a_p, e_p) \\ \hline (b_1, f_1), (b_2, f_2), \dots, (b_q, f_q) \\ \hline \end{array} \right] dt. \end{aligned}$$

Substituting the value of the H-function from (3) in the integrand of (8). we get

$$(9) \quad \begin{aligned} & s^{-1} \int_0^\infty t^l {}_2F_1(a, b; c; -t/s) \times \\ & \times \left[\frac{1}{2\pi i} \int_L^\infty \frac{\prod_{j=1}^m \Gamma(b_j f_j \xi)}{\prod_{j=m+1}^q \Gamma(1 - b_j - f_j \xi)} \frac{\prod_{j=1}^n \Gamma(1 - a_j + e_j \xi)}{\prod_{j=n+1}^p \Gamma(a_j - e_j \xi)} (z s^\sigma)^\xi d\xi \right] dt. \end{aligned}$$

If we interchange the order of integration in (9) and evaluate the t -integral with the help of (1) it reduces to

$$(10) \quad \begin{aligned} & \frac{\Gamma(c)}{\Gamma(a)\Gamma(b)} \cdot \frac{s^l}{2\pi i} \cdot \int_L^\infty \frac{\prod_{j=1}^m \Gamma(b_j - f_j \xi)}{\prod_{j=m+1}^q \Gamma(1 - b_j + f_j \xi)} \frac{\prod_{j=1}^n \Gamma(1 - a_j + e_j \xi)}{\prod_{j=n+1}^p (a_j - e_j \xi)} \times \\ & \times \frac{\Gamma(a - l - 1 - \sigma \xi)}{\Gamma(c - l - 1 - \sigma \xi)} \frac{\Gamma(b - l - 1 - \sigma \xi)}{\Gamma(l + 1 + \sigma \xi)} (z s^\sigma)^\xi d\xi. \end{aligned}$$

On interpreting (10) with the help of (3), we get (5).

The contour L runs from $-i\infty$ to $+i\infty$ such that all the poles of $\Gamma(b_j - f_j \xi)$, $j = 1, 2, \dots, m$; $(a - l - 1 - \sigma \xi)$ and $(b - l - 1 - \sigma \xi)$ are to the right and all the poles of $\Gamma(1 - a_j + e_j \xi)$, $j = 1, 2, \dots, n$ and $(l + 1 + \sigma \xi)$ are to the left of the contour.

Regarding the inversion of the order of integration in (9) we observe that t -integral is absolutely convergent if $(s) > 0$ and $(a - l - 1) > 0$
if $a < b$; $(b - l - 1) > 0$ if $a > b$.

To investigate the convergence of the ξ -integral in (9)

we put $\xi = ix$, $z = Re^{i\theta}$ in it and take the limit as $x \rightarrow \infty$, since [1, page 47]

$$\lim_{|y| \rightarrow \infty} \Gamma(x + iy) = (2\pi)^{\frac{1}{2}} \cdot |y|^{\mu - \frac{1}{2}} \cdot e^{-\frac{1}{2}|y|}$$

the absolute value of the integrand in the ξ -integral is comparable with the expression

$$e^{-\frac{1}{2}\lambda\pi|y|} \cdot |y|^\mu \cdot e^{\theta y}$$

where λ and μ stand for the same quantities as in (5) and $\theta = [\arg(z)]$.

Thus the ξ -integral in (9) is absolutely convergent in at least one of the following conditions

- (i) $\lambda > 0$, $[\arg(z)] < \frac{1}{2}\pi\lambda$
- (ii) $\lambda \geq 0$, $[\arg(z)] < \frac{1}{2}\pi\lambda$ and $(\mu + 1) > 0$.

On obtaining the conditions of absolute convergence of the resulting integral (10) in a manner given above we observe that the inversion of the order of integration in (9) is justified under the conditions stated with the theorem by virtue of de la vallee Poussin's theorem [3, page 504].

Particular cases :

If we put $\sigma = s$ in (5) and further put e 's and f 's equal to s and interpreting the H-function involved with the help of (4), we obtain

$$\begin{aligned} & \int_0^\infty t^l {}_2F_1(a, b; c; -t/s) \times \\ & \quad \times G_{p, q}^{m, n} \left(z^{\frac{1}{s}} t^{\frac{s}{s}} \middle| \begin{matrix} a_1, a_2, \dots, a_p \\ b_1, b_2, \dots, b_q \end{matrix} \right) dt \\ &= \frac{\Gamma(c)}{\Gamma(a)\Gamma(b)} G_{p+2, q+2}^{m+2, n+1} \left(z^{\frac{1}{s}} s^{\frac{s}{s}} \middle| \begin{matrix} -l, a_1, a_2, \dots, a_p, e-l-1 \\ a-l-1, b-l-1, b_1, \dots, b_q \end{matrix} \right). \end{aligned}$$

The conditions of validity can easily be obtained from the conditions of validity of (5).

If we further put $a = c$ and $b = 1$ and slightly adjust the variable we arrive at a known result [2, page 418].

3. Lemmas

The following preliminary lemmas will be needed to establish the recurrence relations of the next section.

Lemma 1 (a) :

If $t F(a \pm 1, b ; c - 1 ; -t/s) \phi(t) \in L(0, \infty)$, $(s) > 0$ and $c \neq 0, -1, -2, -3, \dots$, then

$$(c - a - b) \int_0^\infty F \phi(t) dt + a \int_0^\infty F(a + 1) \phi(t) dt + \\ + s^{-1} \int_0^\infty t F(a + 1) \phi(t) dt - (c - b) \int_0^\infty F(b - 1) \phi(t) dt = 0.$$

where F , $F(a \pm 1)$, and $F(b - 1)$ stand for $F(a, b ; c ; -t/s)$, $F(a \pm 1, b ; c ; -t/s)$ and $F(a, b - 1 ; c, -t/s)$ respectively.

Proof: Since [1, page 103(33)]

$$(c - a - b) F + a (1 - z) F(a + 1) - (c - a) F(b - 1) = 0.$$

Replacing z by $(-t/s)$ and multiplying by $\phi(t)$ and then integrating between $(0, \infty)$, we get the above lemma.

$$(b) \quad (c - 2a) \int_0^\infty F \phi(t) dt + (b - a) s^{-1} \int_0^\infty t F \phi(t) dt + \\ + a \int_0^\infty F(a + 1) \phi(t) dt + a s^{-1} \int_0^\infty t F(a + 1) \phi(t) dt - \\ - (c - a) \int_0^\infty F(a - 1) \phi(t) dt = 0.$$

$$(c) \quad (c - a - 1) \int_0^\infty F \phi(t) dt + a \int_0^\infty F(a + 1) \phi(t) dt - \\ - (c - 1) \int_0^\infty F(c - 1) \phi(t) dt = 0.$$

Proof: To prove (b) and (c) we use the following recurrence relations respectively [1, page 103(31) and (35)],

$$[c - 2a - (b - a) z] F + a (1 - z) F(a + 1) - (c - a) F(a - 1) = 0,$$

$$(c - a - 1) F + a F(a + 1) - (c - 1) F(c - 1) = 0$$

and proceed in a manner similar to that of lemma 1(a).

4. Recurrence relations

Taking

$$\phi(t) = t^l H^{m, n} \left[\begin{array}{c|ccccc} t & (a_1, e_1), & (a_2, e_2), & \dots, & (a_p, e_p) \\ p, q & (b_1, f_1), & (b_2, f_2), & \dots, & (b_q, f_q) \end{array} \right]$$

in lemmas 1(a), (b) and (c) and using (5) we obtain the following recurrence relations respectively after making slight changes in the parameters.

$$\begin{aligned}
(i) \quad & (a_p - b_1 - b_2 + a_1 - 1) \times \\
& \times H_{p, q}^{m, n} \left[x \mid \begin{array}{l} (a_1, e_1), \dots, (a_{p-1}, e_{p-1}), (a_p, e_1) \\ (b_1, e_1), (b_2, e_1), (b_3, f_3), \dots, (b_q, f_q) \end{array} \right] + \\
& + H_{p, q}^{m, n} \left[x \mid \begin{array}{l} (a_1, e_1), (a_2, e_2), \dots, (a_{p-1}, e_{p-1}), (a_p, e_1) \\ (b_1 + 1, e_1), (b_2, e_1), (b_3, f_3), \dots, (b_q, f_q) \end{array} \right] + \\
& + H_{p, q}^{m, n} \left[x \mid \begin{array}{l} (a_1 - 1, e_1), (a_2, e_2), \dots, (a_{p-1}, e_{p-1}), (a_p, e_1) \\ (b_1 + 1, e_1), (b_2 - 1, e_1), (b_3, f_3), \dots, (b_q, f_q) \end{array} \right] - \\
& \quad - (b_2 - a_1) (a_p - b_2) \times \\
& \times H_{p, q}^{m, n} \left[x \mid \begin{array}{l} (a_1, e_1), \dots, (a_{p-1}, e_{p-1}), (a_p, e_1) \\ (b_1, e_1), (b_2 - 1, e_1), (b_3, f_3), \dots, (b_q, f_q) \end{array} \right] = 0
\end{aligned}$$

when $m \geq 2, p \geq n + 1 \geq 3$.

$$\begin{aligned}
(ii) \quad & (b_1 - a_1 + 1) (a_p - a_1 - 2 b_1 - 1) \times \\
& \times H_{p, q}^{m, n} \left[x \mid \begin{array}{l} (a_1, e_1), \dots, (a_{p-1}, e_{p-1}), (a_p, e_1) \\ (b_1, e_1), (b_2, e_1), (b_3, f_3), \dots, (b_q, f_q) \end{array} \right] + (b_1 - a_1 + 1) \times \\
& \times H_{p, q}^{m, n} \left[x \mid \begin{array}{l} (a_1, -e_1), \dots, (a_{p-1}, e_{p-1}), (a_p, e_1) \\ (b_1 + 1, e_1), (b_2, e_1), (b_3, f_3), \dots, (b_q, f_q) \end{array} \right] + \\
& + (b_1 - a_1 + 1) (b_2 - b_1) \times \\
& \times H_{p, q}^{m, n} \left[x \mid \begin{array}{l} (a_1, -1, e_1), (a_2, e_2), \dots, (a_{p-1}, e_{p-1}), (a_p, e_1) \\ (b_1 - 1, e_1), (b_2 - 1, e_1), (b_3, f_3), \dots, (b_q, f_q) \end{array} \right] + \\
& + H_{p, q}^{m, n} \left[x \mid \begin{array}{l} (a_1 - 1, e_1), (a_2, e_2), \dots, (a_{p-1}, e_{p-1}), (a_p, e_1) \\ (b_1, e_1), (b_2 - 1, e_1), (b_3, f_3), \dots, (b_q, f_q) \end{array} \right] - \\
& - (b_1 - a_1 + 1) (a_p - b_1) \times \\
& \times H_{p, q}^{m, n} \left[x \mid \begin{array}{l} (a_1, e_1), \dots, (a_{p-1}, e_{p-1}), (a_p, e_1) \\ (b_1 - 1, e_1), (b_2, e_1), (b_3, f_3), \dots, (b_q, f_q) \end{array} \right] = 0
\end{aligned}$$

when $m \geq 2, p \geq n + 1 \geq 3$.

$$\begin{aligned}
(iii) \quad & (a_p - b_1 - 1) H_{p, q}^{m, n} \left[x \mid \begin{array}{l} (a_1, e_1), \dots, (a_{p-1}, e_{p-1}), (a_p, e_1) \\ (b_1, e_1), (b_2, e_1), (b_3, f_3), \dots, (b_q, f_q) \end{array} \right] + \\
& + H_{p, q}^{m, n} \left[x \mid \begin{array}{l} (a_1, e_1), \dots, (a_{p-1}, e_{p-1}), (a_p, e_1) \\ (b_1 + 1, e_1), (b_2, e_1), (b_3, f_3), \dots, (b_q, f_q) \end{array} \right] + \\
& + H_{p, q}^{m, n} \left[x \mid \begin{array}{l} (a_1, e_1), \dots, (a_{p-1}, e_{p-1}), (a_p - 1, e_1) \\ (b_1, e_1), (b_2, e_1), (b_3, f_3), \dots, (b_q, f_q) \end{array} \right] = 0
\end{aligned}$$

when $m \geq 2, p \geq n + 1$.

Many other recurrence relations can be obtained by using the relations [1, page 103 and 104].

Particular cases :

The following relations for the G-function are obtained by putting a 's and b 's equal to unity in the recurrence relations (i), (ii) and (iii) of the last section.

$$(a_p - b_1 - b_2 + a_1 - 1) G_{p, q}^{m, n} \left(x \left| \begin{matrix} a_1, a_2, \dots, a_p \\ b_1, b_2, \dots, b_q \end{matrix} \right. \right) +$$

$$+ G_{p, q}^{m, n} \left(x \left| \begin{matrix} a_1, a_2, \dots, a_p \\ b_1 + 1, b_2, \dots, b_q \end{matrix} \right. \right) + G_{p, q}^{m, n} \left(x \left| \begin{matrix} a_1 - 1, a_2, \dots, a_p \\ b_1 + 1, b_2 - 1, b_3, \dots, b_q \end{matrix} \right. \right) -$$

$$- (b_2 - a_1) (a_p - b_2) G_{p, q}^{m, n} \left(x \left| \begin{matrix} a_1, a_2, \dots, a_p \\ b_1, b_2 - 1, b_3, \dots, b_q \end{matrix} \right. \right) = 0$$

when $m \geq 2, p \geq n + 1 \geq 2$.

$$(b_1 - a_1 + 1) (a_p - a_1 - 2 b_1 - 1) G_{p, q}^{m, n} \left(x \left| \begin{matrix} a_1, a_2, \dots, a_p \\ b_1, b_2, \dots, b_q \end{matrix} \right. \right) +$$

$$+ (b_1 - a_1 + 1) (b_2 - b_1) G_{p, q}^{m, n} \left(x \left| \begin{matrix} a_1, a_2, \dots, a_p \\ b_1 - 1, b_2 - 1, b_3, \dots, b_q \end{matrix} \right. \right) +$$

$$+ (b_1 - a_1 + 1) G_{p, q}^{m, n} \left(x \left| \begin{matrix} a_1, a_2, \dots, a_p \\ b_1 + 1, b_2, \dots, b_q \end{matrix} \right. \right) +$$

$$+ G_{p, q}^{m, n} \left(x \left| \begin{matrix} a_1 - 1, a_2, \dots, a_p \\ b_1, b_2 - 1, b_3, \dots, b_q \end{matrix} \right. \right) -$$

$$- (b_1 - a_1 + 1) (a_p - b_1) G_{p, q}^{m, n} \left(x \left| \begin{matrix} a_1, a_2, \dots, a_p \\ b_1 - 1, b_2, \dots, b_q \end{matrix} \right. \right) = 0$$

when $m \geq 2, p \geq n + 1 \geq 2$.

$$(a_p - b_1 - 1) G_{p, q}^{m, n} \left(x \left| \begin{matrix} a_1, a_2, \dots, a_p \\ b_1, b_2, \dots, b_q \end{matrix} \right. \right) +$$

$$+ G_{p, q}^{m, n} \left(x \left| \begin{matrix} a_1, \dots, a_p \\ b_1 + 1, b_2, \dots, b_q \end{matrix} \right. \right) + G_{p, q}^{m, n} \left(x \left| \begin{matrix} a_1, \dots, a_{p-1}, a_{p-1} \\ b_1, b_2, \dots, b_q \end{matrix} \right. \right) = 0$$

when $m \geq 2, p \geq n + 1$.

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References

- [1]. Bateman Manuscript Project, Higher Transcendental Fuctions, Vol. I
McGraw Hill, New York, 1953.
- [2]. Bateman Manuscript Project, Tables of Integral Transforms, Vol. II,
McGraw Hill, New York, 1954.
- [3]. Bromwich, T. J. An Introduction to the Theory of Infinite Series.
MacMillan, 1955.
- [4]. Fox, C. The G and H-functions as Symmetrical Fourier kernels.
Trans. Amer. Math. Soc., **98**: 395-429, 1961.

Some Theorems on Fractional Integration, II

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Abstract

The object of the present paper is to obtain few images of confluent hypergeometric functions Φ_1 , Φ_2 , Φ_3 and ψ_1 in Riemann-Liouville (fractional) integral and Weyl (fractional) integrals by using two theorems recently proved by author. Few more connections have been also established between fractional integrals, Varma, and Gauss hypergeometric transforms. This has been done in the form of some theorems which include as particular cases some known results. By using a theorem, the image of H-function in Riemann-Liouville (fractional) integral has also been obtained.

1. We call

$$I_{\mu}^+ f(p) = R_{\mu} \{ f(t) ; p \} = \frac{1}{\Gamma(\mu)} \int_0^p f(t) (p-t)^{\mu-1} dt$$

the Riemann-Liouville (fractional) integral of order μ and

$$K_{\mu}^- f(p) = W_{\mu} \{ f(t) ; p \} = \frac{1}{\Gamma(\mu)} \int_p^{\infty} f(t) (t-p)^{\mu-1} dt$$

the Weyl (fractional) integral of order μ , of $f(t)$ [2, p. 181].

The classical Laplace transform,

$$(1.3) \quad \phi(p) = p \int_0^{\infty} e^{-pt} f(t) dt$$

was generalized by Varma [8, p. 209] in the form,

$$(1.4) \quad \phi(p) = p \int_0^{\infty} e^{-pt} (pt)^{m-\frac{1}{2}} W_{k,m}(pt) f(t) dt,$$

when $k+m = \frac{1}{2}$, (1.4) reduces to (1.3) on account of the well known identity,

$$(1.5) \quad x^{m-\frac{1}{2}} W_{\frac{1}{2}-m,m}(x) = e^{-\frac{1}{2}x}$$

Recently Rajendra Swaroop [7, p. 107] gave a generalization of Stieltjes transform,

$$(1.6) \quad \phi(p) = p \int_0^{\infty} \frac{f(t) dt}{(p+t)\lambda}$$

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in the following form.

$$(1.7) \quad \phi(p) = p^{1-\lambda} \int_0^\infty t^{-\lambda} {}_2F_1\left(\frac{\lambda, \mu}{\nu}; -\frac{t}{p}\right) f(t) dt,$$

when $\mu = \nu$ (1.7) reduces to (1.6).

We shall also use the Gauss-hypergeometric transform in the following form [4, p. 107]

$$(1.8) \quad \phi(p) = p \int_0^\infty t^{-\lambda} {}_2F_1\left(\frac{\lambda, \mu}{\nu}; -\frac{p}{t}\right) f(t) dt$$

When $\mu = \nu$, (1.8) also reduces to (1.6). Symbolically we shall represent (1.3), (1.4), (1.6), (1.7) and (1.8) as,

$$L\{f(t); p\} = \phi(p) \quad V_{k,m}\{f(t); p\} = \phi(p)$$

$$S_\lambda\{f(t); p\} = \phi(p) \quad F\{f(t); \frac{\lambda, \mu}{\nu}; p\} = \varphi(p)$$

and

$$F^*\left\{f(t); \frac{\lambda, \mu}{\nu} p\right\} = \phi(p)$$

respectively.

In a previous paper the author [6] has established connections existing between Riemann-Liouville (fractional) integral, Weyl (fractional) integral and Varma transform. The object of the present paper is to obtain images of confluent hypergeometric functions ϕ_1, ϕ_2, ϕ_3 and ψ_1 in Riemann Liouville (fractional) integral, and Weyl (fractional) integral by using those connections. Further few more connections have been established between fractional integrals, Varma and Gauss-hypergeometric transforms. This has been done in the form of three theorems, which include as particular cases some known results. The image of H-function of Fox [3, p. 408] in Riemann-Liouville (fractional) integral has also been obtained.

The following property of fractional integrals [2, p. 182] will be required in our investigations,

$$(1.9) \quad \int_0^\infty f_1(t) I_\mu^+ f(t) dt = \int_0^\infty K_\mu^- f(t) f_2(t) dt$$

where

$$W_\mu\{f_1(t); p\} = K_\mu^- f(p) \text{ and } R_\mu\{f_2(t); p\} = I_\mu^+ f(p).$$

2. In this section we shall obtain the images of ϕ_1, ϕ_2, ϕ_3 and ψ_1 in Riemann-Liouville (fractional) integral by using the following result recently proved by author, that

If

$$R_\mu\{f(t); p\} = I_\mu^+ f(p)$$

then

$$(2.1) \quad p^{-\mu} L\{f(t); p\} = L\left\{I_\mu^+ f(t); p\right\}$$

provided that the Riemann-Liouville (fractional) integral of $|f(t)|$ exist,

$R(\mu) > 0, R(p) > 0, R(\mu + \xi + 1) > 0$ and $R(\xi + 1) > 0$ where $f(t) = O(t^\xi)$ for small 't'.

Example 1.

If we start with,

$$\text{then [1, p. 222(1)]}. \quad f(t) = t^{\beta-1} \Phi_1(\alpha, \beta + \mu, \gamma; x, yt)$$

$$(2\cdot2) \quad L\{f(t); p\} = \Gamma(\beta) p^{1-\beta} F_1\left(\alpha, \beta + \mu, \beta, \gamma; x, \frac{y}{p}\right)$$

for $R(\beta) > 0, R(p) > 0, R(y),$

using (2·2) in the result (2·1) and then obtaining inverse Laplace transform [1, p. 222] we get,

$$(2\cdot3) \quad R_\mu\{t^{\beta-1} \Phi_1(\alpha, \beta + \mu, \gamma; x, yt); p\} = \frac{\Gamma(\beta)}{\Gamma(\beta + \mu)} p^{\beta + \mu - 1} \Phi_1(\alpha, \beta, \gamma; x, y p)$$

for $R(\beta) > 0, R(\mu) > 0, p > 0.$

Example 2.

If we start with,

$$f(t) = t^{\beta-1} \Phi_2(\beta + \mu, \alpha, \gamma; xt, y)$$

then [1, p. 222(2)]

$$(2\cdot4) \quad \Gamma\{f(t); p\} = \Gamma(\beta) p^{1-\beta} \sum_{n=1}^{\infty} \left(\beta + \mu, \alpha, \beta, \gamma; -\frac{x}{p}, y \right)$$

for $R(p) > 0, R(x) \text{ and } R(\beta) > 0$

using (2·4) in the result (2·1) and then obtaining inverse Laplace transform [1, p. 222] we obtain,

$$(2\cdot5) \quad R_\mu\{t^{\beta-1} \Phi_2(\beta + \mu, \alpha, \gamma; xt, y); p\} = \frac{\Gamma(\beta)}{\Gamma(\beta + \mu)} p^{\beta + \mu - 1} \Phi_2(\alpha, \beta, \gamma; xp, y)$$

for $R(\beta) > 0, R(\mu) > 0 \text{ and } R(p) > 0.$

Example 3.

If we start with,

$$f(t) = t^{\alpha-1} \Phi_3(\alpha + \mu, \gamma; xt, y)$$

then [1, p. 222(6)]

$$(2\cdot6) \quad L\{f(t); p\} = p^{1-\alpha} \Gamma(\alpha) \sum_{n=2}^{\infty} \left(\alpha, \alpha + \mu, \gamma; \frac{x}{p}, y \right)$$

for $R(\alpha) > 0, R(p) > 0, R(x)$

using (2·6) in the result (2·1) and then obtaining inverse Laplace transform [1, p. 222], we get

$$(2\cdot7) \quad R_\mu\{t^{\alpha-1} \Phi_3(\alpha + \mu, \gamma; xt, y); p\} = \frac{\Gamma(\alpha)}{\Gamma(\alpha + \mu)} p^{\alpha + \mu - 1} \Phi_3(\alpha, \gamma; xp, y)$$

for $R(\alpha) > 0, R(\mu) > 0 \text{ and } R(p) > 0.$

Example 4.

Similarly if we take,

$$f(t) = t^{\beta-1} \psi_1(\alpha, \beta + \mu, \gamma, \gamma'; x, yt)$$

then [1, p. 223(11)]

$$(2\cdot8) \quad L\{f(t); p\} = \Gamma(\beta) p^{\beta-1} \beta F_2\left(\alpha, \beta + \mu, \beta, \gamma, \gamma'; x, \frac{y}{p}\right),$$

$$R(\beta) > 0, R(p) > 0, R(y).$$

using (2·8) in (2·1) and then obtaining the inverse Laplace transform [1, p. 223] we get,

$$(2\cdot9) \quad R_\mu\{t^{\beta-1} \psi_1(\alpha, \beta + \mu, \gamma, \gamma'; x, yt); p\} = \frac{\Gamma(\beta)}{\Gamma(\beta + \mu)} p^{\mu+\beta-1} \psi_1(\alpha, \beta, \gamma, \gamma'; x, y\frac{p}{\beta}).$$

for $R(\beta) > 0, R(\mu) > 0$ and $R(p) > 0$.

3. In this section we shall obtain the images of Φ_1, Φ_2, Φ_3 and ψ_1 in Weyl (fractional) integral by using the following result recently proved by author, [6] that,

If

$$W_\mu \left\{ f\left(\frac{1}{t}\right), p \right\} = K_\mu^- f(p)$$

then

$$(3\cdot1) \quad p^{-\mu} L\{t^{-\mu-1} f(t); p\} = L\left\{ t^{\mu-1} K_\mu^- f\left(\frac{1}{t}\right); p\right\}$$

Provided that the Weyl (fractional) integral of $|f\left(\frac{1}{t}\right)|$ exist. $R(\mu) > 0$,

$R(p) > 0$ and $R\left(\xi - \frac{\mu}{2} \pm \frac{\mu}{2}\right) > 0$ where $f(t) = 0 (t^\xi)$ for small 'v'.

Example 1.

If we start with,

$$f(t) = t^{\beta-1} \Phi_1(\alpha, \beta - 1, \gamma; x, yt)$$

then [1, p. 222(1)]

$$(3\cdot2) \quad L\{t^{-\mu-1} f(t); p\} = \Gamma(\beta - \mu - 1) p^{2+\mu-\beta} F_1\left(\alpha, \beta - 1, \beta - \mu - 1; \gamma; x, \frac{y}{p}\right)$$

for $R(\beta - \mu - 1) > 0, R(p) > 0, R(y)$

using (3·2) in the result (3·1) and then obtaining inverse Laplace transform [1, p. 222] we get

$$(3\cdot3) \quad W_\mu\{t^{1-\beta} \Phi_1(\alpha, \beta - 1, \gamma; x, yt); p\} = \frac{\Gamma(\beta - \mu - 1)}{\Gamma(\beta - 1)} p^{1+\mu-\beta} \Phi_1\left(\alpha, \beta - \mu - 1; \gamma; x, \frac{y}{p}\right)$$

for $R(\beta - \mu - 1) > 0, R(\mu) > 0, R(p) > 0$.

Example 2.

If we start with,

$$f(t) = t^{\beta-1} \Phi_2(\beta - 1, \alpha, \gamma; xt, y)$$

then [1, p. 222(2)]

$$(3\cdot4) \quad L\{f(t); p\} = \Gamma(\beta - \mu - 1) p^{2+\mu-\beta} F_{1,1}\left(\beta - 1, \alpha, \beta - \mu - 1, \gamma; x, \frac{y}{p}\right)$$

for $R(\beta - \mu - 1) > 0, R(p) > 0, R(\mu) > 0$

using the result (3.4) in (3.1) and then obtaining the inverse Laplace transform [1, p. 222] we get

$$(3.5) \quad W_\mu \left\{ t^{1-\beta} \Phi_2 \left(\beta - 1, \alpha, \gamma ; \frac{x}{t}, y \right); p \right\} = \frac{\Gamma(\beta - \mu - 1)}{\Gamma(\beta - 1)} p^{1+\mu-\beta} \Phi_2 (\alpha, \beta - \mu - 1, \gamma; \frac{x}{p}, y)$$

for $R(\beta - \mu - 1) > 0, R(\mu) > 0, R(p) > 0.$

Example 3.

If we start with,

$$f(t) = t^{\alpha-1} \Phi_3 (\alpha - 1, \gamma; xt, y)$$

then [1, p. 222(6)]

$$(3.6) \quad L \left\{ t^{\mu-1} f(t); p \right\} = \Gamma(\alpha - \mu - 1) p^{2+\mu-\alpha} F_2 \left(\alpha - \mu - 1, \alpha - 1, \gamma; \frac{x}{p}, y \right)$$

for $R(\alpha - \mu - 1) > 0, R(\mu) > 0, R(p) > 0$

using (3.6) in the result (3.1) and then obtaining inverse Laplace transform [1, p. 222] we get

$$(3.7) \quad W_\mu \left\{ t^{1-\alpha} \Phi_3 \left(\alpha - 1, \gamma; \frac{x}{t}, y \right); p \right\} = \frac{\Gamma(\alpha - \mu - 1)}{\Gamma(\alpha - 1)} p^{1+\mu-\alpha} \Phi_3 \left(\alpha - \mu - 1, \gamma; \frac{x}{p}, y \right)$$

for $R(\alpha - \mu - 1) > 0, R(\mu) > 0, R(p) > 0.$

Example 4.

Similarly if we take,

$$f(t) = t^{\beta-1} \psi_1 (\alpha, \beta - 1, \gamma, \gamma'; x, yt)$$

then [1, p. 222(11)]

$$(3.8) \quad L \left\{ t^{\mu-1} f(t); p \right\} = \Gamma(\beta - \mu - 1) p^{2+\mu-\beta} F_2 \left(\alpha, \beta - 1, \beta - \mu - 1; \gamma, \gamma'; x, \frac{y}{p} \right)$$

$R(\beta - \mu - 1) > 0, R(\mu) > 0, R(p) > 0$

using (3.8) in the result (3.1) and then obtaining inverse Laplace transform we obtain,

$$(3.9) \quad W_\mu \left\{ t^{1-\beta} \psi_1 \left(\alpha, \beta - 1, \gamma, \gamma'; x, \frac{y}{t} \right); p \right\} = \frac{\Gamma(\beta - \mu - 1)}{\Gamma(\beta - 1)} p^{\mu - \beta + 1} \psi_1 \left(\alpha, \beta - \mu - 1, \gamma, \gamma'; x, \frac{y}{p} \right)$$

for $R(\beta - \mu - 1) > 0, R(\mu) > 0, R(p) > 0.$

4. In this section we shall establish the relationship existing between the Riemann-Liouville (fractional) integral and Varma transform. This has been done in the form of a theorem which has been illustrated with an example, so as to give the Riemann-Liouville (fractional) integral of H-function of Fox [3, p. 498].

Theorem 1.

If

$$(4 \cdot 1) \quad R_\mu \{ f(t) ; p \} = I_\mu^+ f(p)$$

then

$$(4 \cdot 2) \quad V_{k, \lambda} \{ t^{k-\mu-\lambda-\frac{1}{2}} I_\mu^+ f(t) ; p \} = V_{k-\mu, \lambda} \{ t^{k-\lambda-\frac{1}{2}} f(t) ; p \}$$

for $R(\mu) > 0, R(p) > 0$ and $R(k + \frac{1}{2} \pm \lambda + \xi) > 0$ where $f(t) = 0$ ($t^{\frac{1}{2}}$) for small t .

Proof:

We have [2, p. 211]

$$(4 \cdot 3) \quad W_\mu \{ t^{\rho-\mu-1} e^{-\frac{1}{2}at} W_{k, \lambda} (at) ; p \} = p^{\lambda-1} e^{-\frac{1}{2}ap} W_{k-\mu, \lambda} (\alpha p), \\ R(\mu) > 0, R(\alpha p) > 0.$$

using the relations (4·1) and (4·3) in (1·9) we get (4·2) after a little simplification.

Example

If we take

$$f(t) = t^{\rho-\mu} H_{l, q}^{m, n} \left[zt^\sigma \begin{array}{|c} (a_1, e_1), \dots, (a_l, e_l) \\ (b_1, f_1), \dots, (b_q, f_q) \end{array} \right]$$

then [5, p. 99]

$$(4 \cdot 4) \quad = p^{\lambda+\mu-k-\rho+\frac{3}{2}} H_{l+2, q+1}^{m, n+2} \left[zp^{-\sigma} \begin{array}{|c} (\frac{1}{2}-\rho-k+\mu \pm \lambda; \sigma), (a_1, e_1), \dots, (a_l, e_l) \\ (b_1, f_1), \dots, (b_q, f_q), (-\rho, \sigma) \end{array} \right]$$

for $\sigma > 0, 0 \leq m \leq q, 0 \leq n \leq l, R(\mu) > 0, \lambda > 0$

$$\text{and } R \left(k + \rho - \mu \pm \lambda + \frac{1}{2} + \sigma \min \frac{b_h^h}{f_h} \right) > 0 \{ h = 1, \dots, m \}$$

using (4·4) in (4·2) and then obtaining the inverse Laplace transform [5, p. 99] we get,

$$R_\mu \left\{ t^{\rho-\mu} H_{l, q}^{m, n} \left[zt^\sigma \begin{array}{|c} (a_1, e_1), \dots, (a_l, e_l) \\ (b_1, f_1), \dots, (b_q, f_q) \end{array} \right]; p \right\} \\ = p^\rho H_{l+1, q+1}^{m, n+1} \left[zp^\sigma \begin{array}{|c} (\mu - \rho, \sigma), (a_1, e_1), \dots, (a_l, e_l) \\ (b_1, f_1), \dots, (b_q, f_q), (-\rho, \sigma) \end{array} \right],$$

for $R(p) > 0, \sigma > 0, 0 \leq m \leq q, 0 \leq n \leq l, R(\mu) > 0$

and $R(bj + 1) > 0 \{ j = 1, \dots, m \}$.

If we take $e_1 = \dots = e_l = f_1 = \dots = f_q = \sigma = 1$ then we obtain a known result [2, p. 200].

5. In this section we shall establish connections between Riemann–Liouville (fractional) integral, Weyl (fractional) integral and Gauss-hypergeometric transforms.

Theorem 2.

If

$$(5 \cdot 1) \quad R_\mu \{ f(t) ; p \} = I_\mu^+ f(p)$$

then

$$(5 \cdot 2) \quad S_\nu \left\{ t^{-\lambda} I_\mu^+ f(t) ; p \right\} = \frac{\Gamma(\lambda - \mu + \nu)}{\Gamma(\lambda + \nu)} F* \left\{ f(t) ; \lambda - \mu + \nu, \nu ; \lambda + \nu ; p \right\}$$

for $0 < R(\mu) < R(\lambda + \nu)$ and $R(1 - \lambda - \nu + \xi) > 0$, where $f(t) = 0 (t^\xi)$ for small ‘ t ’.

Proof :

We have [2, p. 201(8)]

$$(5 \cdot 3) \quad W_\mu \{ t^{-\lambda} (t + a)^{-\nu} ; p \} = \frac{\Gamma(\lambda - \mu + \nu)}{\Gamma(\lambda + \nu)} p^{\mu - \nu - \lambda} {}_2F_1 \left(\begin{matrix} \lambda - \mu + \nu, \nu \\ \lambda + \nu \end{matrix} ; - \frac{a}{p} \right)$$

for $0 < R(\mu) < R(\lambda + \nu)$, $\left| \arg \left(\frac{a}{p} \right) \right| < \pi$,

using (5·1) and (5·3) in (1·9) we get (5·2) after a little simplification.

Corollary : If we take $\lambda = 0$, in the above theorem on Gauss-hypergeometric transform, we obtain a well known theorem on Stieltjes transform [2, p. 233(7)] in the following form,

If

$$R_\mu \{ f(t) ; p \} = I_\mu^+ f(p)$$

then

$$(5 \cdot 4) \quad S_\nu \left\{ I_\mu^+ f(t) ; p \right\} = \frac{\Gamma(\nu - \mu)}{\Gamma(\nu)} S_{\nu - \mu} \{ f(t) ; p \}$$

for $0 < R(\mu) < R(\nu)$.

Theorem 3.

If

$$(5 \cdot 5) \quad W_\mu \{ f(t) ; p \} = K_\mu^- f(p)$$

then

$$(5 \cdot 6) \quad S_\lambda \left\{ t^{\nu-1} K_\mu^- f(t) ; p \right\} = \frac{\Gamma(\nu)}{\Gamma(\mu + \nu)} p^{\nu - \lambda} F \left\{ t^{\mu + \nu - 1} f(t) ; \frac{\lambda, \nu}{\mu + \nu} ; p \right\}$$

$R(\mu) > 0$, $R(\nu) > 0$, $R(\mu + \nu + \xi) > 0$ where $f(t) = 0 (t^\xi)$ for small ‘ t ’, $R(\lambda - \mu - \nu - \eta) > 0$, $R(\mu + \eta) < 0$ where $f(t) = 0 (t^\eta)$ for large ‘ t ’.

Proof : We have [2, p. 186(9)]

$$(5.7) \quad R_\mu \{ t^{\nu-1} (t+a)^{-\lambda} ; p \} = \frac{a^{-\lambda} p^{\mu+\nu-1} \Gamma(\nu)}{\Gamma(\mu+\nu)} {}_2F_1 \left(\begin{matrix} \lambda, \nu \\ \mu + \nu \end{matrix}; -\frac{p}{a} \right),$$

$$R(\mu) > 0, R(\nu) > 0 \text{ and } \left| \arg \frac{p}{a} \right| < \pi$$

using (5.5) and (5.7) in (1.9) we get (5.6) after a little simplification.

Corollary : If we take $\lambda = \mu + \nu$ in the above theorem on Gauss-hypergeometric transform, then we obtain a theorem on Stieltjes transform in the following form :

If

$$W_\mu \{ f(t) ; p \} = K_\mu^- f(p)$$

then

$$(5.8) \quad S_{\mu+\nu} \left\{ t^{\nu-1} K_\mu^- f(t) ; p \right\} = \frac{\Gamma(\nu)}{\Gamma(\mu+\nu)} S_\nu \{ t^{\mu+\nu-1} f(t) ; p \}$$

$$R(\mu) > 0, R(\nu) > 0, R(\mu + \nu + \xi) > 0 \text{ where } f(t) = 0 (t^\xi)$$

for small 't' and $R(\mu + \nu) < 0$ where $f(t) = 0 (t^\eta)$ for large 't'.

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References

1. Erdelyi, A. et al. Tables of integral transforms, Vol. I. *McGraw-Hill, New York*, 1954.
2. ——— Tables of integral transforms, Vol. II. *McGraw-Hill, New York*, 1954.
3. Fox, C. The G and H-functions as symmetrical Fourier Kernels, *Trans. Amer. Math. Soc.*, **98**, 395-429, 1961.
4. Gokhroo, D. C. Some complex inversion formulae for the generalized Stieltjes transform, *Annales de la Soc. Sci. de Bruxelles*, **79**, 107-112, 1965.
5. Gupta, K. C. On the H-function. *Annales de la Soc. Sci. de Bruxelles*, **79**, 97-106, 1965.
6. Kalla, S. L. Some theorems on fractional integration. *Proc. Nat. Acad. Sci. India*. Vol. 36 (IV) 1007-1012, 1966.
7. Swaroop, Rajendra. On a generalization of the Laplace and the Stieltjes transforms. *Annales de la Soc. Sci. de Bruxelles*, **78**, 105-112, 1964.
8. Varma, R. S. On a generalization of Laplace integral. *Proc. Nat. Acad. Sci., India*, **20**, 209-216, 1951.

Chemical Examination of the Plant *Pterospermum acerifolium* Study of the Seed Oil

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Abstract

The oil from the seed of *Pterospermum acerifolium*¹ (N.O. Sterculaceae) has been found to contain the following fatty acids : oleic 37·12%, linoleic 29·58%, behenic 5·81%, arachidic 9·46%, stearic 8·23%, palmitic 5·97% and myristic 3·74%. The unsaponified matter is found to be mixture of three compounds, which have been separated by column chromatography and identified as β -amyrin and β - and γ -sitosterol.

Experimental

4 Kg of air dried and powdered seeds were extracted with petroleum ether (40–60°) in a soxhlet extractor. The solvent was removed from the extract and when kept overnight in a refrigerator it gave a semi-solid waxy deposit which was separated by filtration. The oil thus obtained after removing the deposit was 600 gms (15% of the seed).

Study of the deposit : The petroleum ether soluble part of the deposit showed positive Liebermann-Burchard reaction. This was separated into two fractions (A and B) by column chromatography. Fraction A on crystallisation from methanol gave a colourless crystalline substance, γ -sitosterol, m.p. 148°, $[\alpha]_D^{25} \sim -48^\circ$ (CHCl_3). The fraction B on crystallisation from methanol gave another solid, β -sitosterol, m.p. 137°, $[\alpha]_D^{25} \sim -35^\circ$ (CHCl_3). The petroleum ether insoluble part of the deposit was crystallised from a mixture of chloroform : methanol (1 : 1) in needle-shaped crystals, m.p. 199–200°. Found (C=84·38, H=11·85%), $[\alpha]_D^{25} + 85·5^\circ$ (CHCl_3), calculated for $\text{C}_{30}\text{H}_{50}\text{O}$, (C=84·51, H=11·74%). The compound was identified as β -amyrin by mixed m.p.

The oil (S. V. = 200·45, I. V. = 80·60) was saponified by refluxing it with alcoholic KOH and the mixed fatty acids were recovered by the usual procedure. 200 gms of the mixed fatty acids were segregated into solid and liquid fatty acids by Twitchell² lead salt alcohol process as modified by Hilditch³ and coworkers. They were found to have the following constants.

TABLE I

Franciton	Weight	Saponification value	Iodine value
Solid	52 gms 26%	200·53	1·52
Liquid	148 gms 74%	200·16	109·85

The solid and liquid acids were further fractionated into their components by urea adduct⁴ formation method. A qualitative study of solid and liquid acids in each fractions was done by paper chromatography^{5,6,7,8}.

TABLE 2
Fractionation of solid acids with urea :
 Weight 26 gms, S. V. = 200.53, I. V. = 1.52

Adduct.	Wt of the fraction	S.V.	S.E.	I.V.	Behenic	Arachidic	Stearic	Palmitic	Myristic	Oleic
S 1	4.20	168.30	333.33	1.21	3.210	0.933	-	-	-	0.057
S 2	3.64	170.62	328.80	1.01	1.983	1.615	-	-	-	0.042
S 3	3.79	184.59	303.91	1.14	-	2.603	1.139	-	-	0.048
S 4	3.20	184.07	304.76	1.63	-	1.924	1.218	-	-	0.058
S 5	2.66	187.13	299.94	1.89	-	1.281	1.323	-	-	0.056
S 6	2.14	205.26	273.30	1.59	-	-	1.045	1.057	-	0.538
S 7	1.78	216.83	258.72	1.26	-	-	-	1.755	-	0.025
S 8	1.60	238.43	235.29	-	-	-	-	0.436	1.164	-
S 9	1.15	239.03	234.69	5.16	-	-	-	-	1.084	0.066
Raffinate										
S 10	0.90	211.09	264.70	26	-	-	-	0.325	0.315	0.26
Total Wt.	25.06				5.139gm,	8.354,	4.725,	3.573,	2.563,	0.650
%acid in solid fraction.					20.72	33.34	18.55	14.25	10.22	2.59

TABLE 3
Fractionation of liquid acids with urea :
 Weight = 36 gms, S. V. = 201.16, I. V. = 109.85

Adduct	Weight (gm)	S. V.	S. E.	I. V.	Oleic	Linoleic	Behenic	Arachidic	Stearic	Palmitic	Myristic
L 1	4.29	197.50	283.92	103.34	2.08	1.95	0.21	-	-	-	-
L 2	3.70	198.56	282.52	120.89	2.11	1.43	-	0.16	-	-	-
L 3	3.35	201.50	278.40	118.53	1.66	1.37	-	-	0.32	-	-
L 4	2.94	199.45	281.27	122.75	1.35	1.33	-	-	0.26	-	-
L 5	2.68	199.47	281.24	124.25	1.32	1.19	-	-	0.17	-	-
L 6	2.14	215.15	249.16	100.51	0.93	0.73	-	-	-	0.26	0.22
L 7	1.88	201.72	278.10	117.76	0.86	0.80	-	-	-	0.22	-
L 8	1.14	202.23	277.40	97.88	0.44	0.40	-	-	0.12	0.18	-
L 9	0.76	208.98	268.44	93.55	0.37	0.21	-	-	-	-	0.18

(contd.)

Raffinate

L 18	3.00	200.51	279.78	114.00	1.34	1.23	-	-	0.25	0.18	-
L 17	2.58	197.83	283.51	103.25	1.26	0.85	-	-	0.24	0.23	-
L 16	2.03	197.41	284.18	115.71	1.05	0.78	-	0.20	-	-	-
L 15	1.80	199.39	281.37	118.00	0.96	0.70	-	-	0.14	-	-
L 14	1.65	199.37	281.38	117.81	0.88	0.64	-	-	0.13	-	-
L 13	0.75	204.92	273.76	91.20	0.52	0.12	-	-	-	-	0.11
L 12	0.24	-	-	146.25	0.09	0.15	-	-	-	-	-
L 11	0.19	-	-	135.00	0.05	0.14	-	-	-	-	-
L 10	0.14	-	-	-	-	-	-	-	-	-	-
Total Wt.	35.07 gm				17.27	14.02	0.21	0.36	1.63	1.07	0.51
% acid in liquid fraction					49.24	39.98	0.6	1.03	4.64	1.05	1.45

The percentage of each acid in mixed acid has been found with the help of Table 1, 2 and 3, and the results are recorded in Table 4.

TABLE 4

Acid	% in solid acids	% in liquid acids	% in mixed fatty acids
Oleic	2.59	49.24	37.12
Linoleic	-	39.98	29.58
Behenic	20.72	0.6	5.81
Arachidic	33.34	1.03	9.46
Stearic	18.85	4.64	8.23
Palmitic	14.25	3.05	5.97
Myristic	10.22	1.45	3.74

References

- Chopra, R. N., Nayer, S. L. and Chopra, I. C. "Glossary of Indian Medicinal Plants." C. S. I. R. New Delhi, Ed. Page 206, 1956.
- Twitchell, E. J. *Ind. Eng. Chem.* **13**, 806, 1925.
- Hilditch, J. P. Chemical Constitution of Natural Fats. Chapman and Hall, 3rd Edition 577, 1956.
- Tandon, S. P. and Tiwari, K. P. *National Academy Sciences*, Vol. 36 Sec. A Part III (in Press)
- Inouye, X. and Noda, M. *J. Agr. Chem. Soc., Japan*, **26**, 634, 1952.
- Ibid ; **27**, 50, 1953.
- Spirer., J. *Bull. Soc. Chem., Biol.*, **36**, 1355, 1954.
- A Manual of Paper Chromatography and Paper Electrophoresis by Block, Durrum and Swig, Second Edition 244, 1958.

Neutralization of phosphoric acid with barium and strontium carbonates

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Abstract

Some marked similarities have been observed between the behaviour of barium and strontium carbonates with the solutions of phosphoric acid. Barium carbonate appears to be more reactive than strontium carbonate.

The electric conductivity falls gradually in both the systems when carbonates of barium and strontium are added to phosphoric in the increasing ratio of carbonate : P_2O_5 of 1 : 1, 2 : 1 and 3 : 1. In all the phosphoric acid concentrations the conductivity changes are more marked in the case of barium carbonate system than with strontium carbonate system. The pH measurements show that the adsorption of hydrogen ions is comparatively greater with barium system than with strontium system.

The formation of dibasic salt takes place invariably, when barium and strontium carbonates are added to phosphoric acid in the carbonate : P_2O_5 ratio of 1 : 1 and 2 : 1. The best yield of dibarium phosphate is obtained with 0.2M concentration of the acid and of distrontium phosphate with 5M concentration of the acid, when carbonates are added to phosphoric acid in the molecular ratio of carbonate : P_2O_5 as 2 : 1.

It has been found that complete neutralization of phosphoric acid takes place when barium and strontium carbonates are added to phosphoric acid in the molecular ratio of carbonate : P_2O_5 as 3 : 1. The maximum efficiency of precipitation of tribarium phosphate is obtained with 0.2M phosphoric acid and of tristrontium phosphate with M phosphoric acid.

Introduction

Among calcium, strontium and barium phosphates emphasis has been laid only on the preparations of calcium phosphates and very little work has been done on barium and strontium phosphates. Various modifications of the early methods have been put forward suggesting improvements and avoiding presence of impurities.

In this paper an attempt has been made to study the neutralization of phosphoric acid by barium and strontium carbonates at 30°C.

Experimental

Extra pure phosphoric acid and A. R. quality of barium and strontium carbonates were used in these experiments. 25 ml standard solutions of phosphoric acid concentrations 5M, M, 0·2M and 0·04M were taken in 250 ml Jena glass bottles and barium and strontium carbonates were added in the molecular ratio of carbonate : P_2O_5 as 1 : 1, 2 : 1 and 3 : 1 at 30°C. While adding carbonates the solutions were vigorously shaken and the rise in temperature was noted in every case. The contents were shaken in a mechanical shaker for one hour and then left over for 24 hours in a thermostat at 20°C. Next day the solid was drained by suction in a sintered crucible and the filtrate collected. The solid was thoroughly washed with acetone and finally three or four times with ether. It was air dried and weighed. A portion of the solid was dissolved in dilute hydrochloric acid and the solution made upto a definite volume. Aliquot portions of the solutions were utilized for the analysis of the ingredients. The electrical conductivity and pH determinations of the filtrates were also carried out at 30°C.

Observations

TABLE I

Concentra- tion of the acid	Molecular ratio of carbonate : P_2O_5	Initial specific conductiv- ty in mhos $\times 10^{-4}$	Specific conductivity		Initial pH of the acid	pH of filtrate	
			Ba system	Sr system		Ba system	Sr system
5M	1 : 1	1830·00	623·20	695·70	0·40	1·95	1·85
	2 : 1		65·10	68·40		3·15	4·85
	3 : 1		No filtrate obtained	No filtrate obtained		No filtrate obtained	No filtrate obtained
M	1 : 1	488·00	200·80	253·50	0·80	2·40	2·10
	2 : 1		27·60	54·60		4·85	4·50
	3 : 1		4·32	4·82		8·75	8·10
0·2 M	1 : 1	146·80	79·20	82·80	1·40	2·95	2·85
	2 : 1		3·54	43·80		5·85	0·95
	3 : 1		3·02	3·04		8·45	7·80
0·04M	1 : 1	51·80	28·60	31·30	2·05	3·45	3·25
	2 : 1		2·02	22·20		6·40	3·75
	3 : 1		1·27	1·86		8·05	7·65

TABLE 2

Concentration of phosphoric acid	Molecular ratio of $\text{BaCO}_3 : \text{P}_2\text{O}_5$	Rise in temperature in °C	P_2O_5 %	BaO %	Nature of residue
5M	1 : 1	6.5	31.46	66.88	BaHPO_4
	2 : 1	6.5	30.37	66.02	BaHPO_4
	3 : 1	6.5	22.86	72.77	$\text{Ba}_3(\text{PO}_4)_2 \cdot 1 \cdot 5\text{H}_2\text{O}$
M	1 : 1	4.5	30.53	65.94	BaHPO_4
	2 : 1	5.0	30.01	65.58	BaHPO_4
	3 : 1	5.5	22.60	72.36	$\text{Ba}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$
0.2M	1 : 1	3.0	29.87	65.13	BaHPO_4
	2 : 1	3.0	29.73	64.92	BaHPO_4
	3 : 1	3.5	22.38	71.90	$\text{Ba}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$
0.04M	1 : 1	0.5	29.19	64.03	$\text{BaHPO}_4 \cdot 1/2 \text{H}_2\text{O}$
	2 : 1	1.0	29.08	63.88	$\text{BaHPO}_4 \cdot 1/2 \text{H}_2\text{O}$
	3 : 1	1.0	22.18	70.52	$\text{Ba}_3(\text{PO}_4)_2 \cdot 2 \cdot 5\text{H}_2\text{O}$

TABLE 3

Concentration of phosphoric acid	Molecular ratio of $\text{SrCO}_3 : \text{P}_2\text{O}_5$	Rise in temperature in °C	P_2O_5 %	SrO %	Nature of residue
5M	1 : 1	5.5	39.23	57.44	SrHPO_4
	2 : 1	5.5	38.97	56.95	SrHPO_4
	3 : 1	6.0	29.49	65.46	$\text{Sr}_3(\text{PO}_4)_2 \cdot 1 \cdot 5\text{H}_2\text{O}$
2M	1 : 1	3.0	39.02	57.11	SrHPO_4
	2 : 1	3.5	31.78	56.62	SrHPO_4
	3 : 1	4.0	29.26	64.93	$\text{Sr}_3(\text{PO}_4)_2 \cdot 1 \cdot 5\text{H}_2\text{O}$
0.2M	1 : 1	1.0	38.75	56.65	SrHPO_4
	2 : 1	1.5	38.39	56.38	SrHPO_4
	3 : 1	2.0	29.05	63.96	$\text{Sr}_3\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$
0.04M	1 : 1	0.5	-	-	No residue obtained
	2 : 1	0.5	37.80	55.93	SrHO_4
	3 : 1	1.0	28.88	63.50	$\text{Sr}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$

TABLE 4

Concentration of phosphoric acid	Molecular ratio of carbonate : P_2O_5	Amount of carbonate added in gms		Amount of product formed in gms	
		$BaCO_3$	$SrCO_3$	Ba system	Sr system
5M	1 : 1	12.3350	9.2266	12.6568	97.042
	2 : 1	24.6700	18.4530	27.0004	21.8175
	3 : 1	37.0050	27.6796	37.9902	29.2100
M	1 : 1	2.4670	1.8454	1.9310	1.0576
	2 : 1	4.9340	3.6906	5.4544	4.2330
	3 : 1	7.4010	5.5360	7.6776	5.9488
0.2M	1 : 1	0.4934	0.3690	0.1734	0.1592
	2 : 1	0.9868	0.7380	1.1112	0.7310
	3 : 1	1.4802	1.1070	1.5498	1.1916
0.04M	1 : 1	0.0986	0.0738	0.0302	No residue obtained
	2 : 1	0.1972	0.1476	0.2216	0.1128
	3 : 1	0.2958	0.2214	0.3132	0.2410

TABLE 5

Concentration of phosphoric acid	Molecular ratio of carbonate : P_2O_5	Percentage of P_2O_5 used up		Percentage efficiency of precipitation	
		Ba system	Sr system	Ba system	Sr system
5M	1 : 1	45.66	35.56	86.79	68.87
	2 : 1	94.04	97.50	92.62	95.05
	3 : 1	99.58	98.80	96.62	97.38
M	1 : 1	33.80	23.77	66.19	46.07
	2 : 1	93.85	94.12	93.49	92.21
	3 : 1	99.49	99.80	96.25	99.16
0.2M	1 : 1	14.85	14.81	29.72	34.68
	2 : 1	94.69	80.45	95.23	79.61
	3 : 1	99.45	99.24	97.15	97.49
0.04M	1 : 1	12.59	-	24.93	-
	2 : 1	92.37	61.22	91.49	61.43
	3 : 1	99.58	99.77	96.81	98.60

Discussion

The foregoing observations clearly show some marked similarities between the behaviour of barium and strontium carbonates with the solutions of phosphoric acid. Barium carbonate appears to be more reactive than strontium carbonate.

The electric conductivity has been found to fall gradually in both the cases, when carbonates of barium and strontium are added to phosphoric acid in the increasing ratio of 1 : 1, 2 : 1 and 3 : 1. The conductivity changes are more marked in the case of barium system than with strontium system in all the

phosphoric acid concentrations. It is evident that more ions are disappearing from solutions of phosphoric acid in which barium carbonate is added than in the case of strontium carbonate. In both the systems the maximum number of ions are removed when carbonates are added to phosphoric acid in the molecular ratio of carbonate : P_2O_5 ratio of 3 : 1 and minimum when added in the ratio of 1 : 1.

The results show that when barium and strontium carbonates are added to phosphoric acid in the carbonate : P_2O_5 ratio of 1 : 1, the whole of the added amounts do not dissolve, but some solid residue remains. Only with 0·04M acid concentration in the case of strontium carbonate the whole of the added amount has dissolved. In both the systems of the formation of secondary phosphate has taken place instead of primary phosphate. The ratio of oxide : P_2O_5 in the solid is invariably 2 : 1. With strontium carbonate anhydrous salt has been formed in every case, but with barium carbonate in 0·04M acid concentration $BaHPO_4 \cdot 1/2 H_2O$ has precipitated and in rest of the concentrations anhydrous salt is formed. It has been observed that the percentage amount of P_2O_5 used up in the reaction decreases with the dilution in the concentration of the acid in both the systems. It can be seen that the amount of P_2O_5 spent in the reaction is always greater with $BaCO_3$ - H_3PO_4 system than with $SrCO_3$ - H_3PO_4 system with the same concentration of the acid. The pH measurements show that the adsorption of hydrogen ions is comparatively greater with barium system than with strontium system.

When barium and strontium carbonates are added to phosphoric acid in the carbonate : P_2O_5 ratio of 2 : 1, the formation of dibasic salt takes place invariably. It is interesting to note that the compositions of the products formed are similar to the products obtained, when barium and strontium carbonates are added to phosphoric acid in the carbonate : P_2O_5 ratio of 1 : 1. The percentage amount of P_2O_5 that is used up in the reaction remains practically the same in the case of barium carbonate system, but in the case of strontium carbonate system the percentage decreases with the lowering in the concentration of the acid.

When barium and strontium carbonates are added to phosphoric acid in the carbonate : P_2O_5 ratio of 3 : 1, it has been observed that tribasic salt has been precipitated in both the cases. It is evident from the results that there is complete neutralization of phosphoric acid when barium and strontium carbonates are added to phosphoric acid in the molecular ratio of 3 : 1. It appears that the degree of hydration increases with the dilution in the concentration of the acid. The pH of the solutions is always on the alkaline side in both the systems, indicating that there is more of base than P_2O_5 remaining in the solution.

The specific conditions under which the maximum yield of the products formed is obtained may now be taken into account. The percentage efficiency of formation of dibarium phosphate from 5M, M, 0·2M and 0·04M phosphoric acid concentrations is 92·62, 93·49, 95·23 and 91·49 respectively and of distrontium phosphate is 95·05, 92·21, 79·61 and 61·43 respectively, when carbonates are added in the molecular ratio of carbonate : P_2O_5 as 2 : 1. From these figures it is evident that maximum efficiency of precipitation of dibarium phosphate is obtained at 0·2M phosphoric acid concentration and of distrontium phosphate at 5M acid concentration. The percentage efficiency of formation of tribasic barium phosphate with 5M, M, 0·2M and 0·04M phosphoric acid concentrations is 96·62, 96·25, 97·15 and 96·81 respectively and of tribasic strontium phosphate is 97·38, 99·16, 97·49 and 98·60 respectively. From these figures the best yield of tribarium phosphate is obtained at 0·2M concentration of the acid and of tristrontium acid in the molecular ratio of carbonate : P_2O_5 as 3 : 1.

On Flexural Vibrations of a Viscoelastic Rod In a Magnetic Field

By

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Abstract

This paper makes use of the equations of rotatory and transverse motion for a viscoelastic rod permeated by a magnetic field to investigate the flexural vibrations of the rod with the help of classical methods of elasticity and electromagnetism.

1. Introduction

The study on the interactions of electromagnetic fields with mechanical fields is of recent origin and is chiefly relevant to various branches of engineering and technology, for example, in aero-magnetic flutter, in the detection of mechanical explosions inside the earth. Moreover, the research on these interactions can be attributed largely to the reappraisal of well-known mechanical problems—elastic or viscoelastic—in the presence of magnetic field, for such fields provide a source of damping of the dynamical characteristics of the materials concerned, apart from those mechanical parameters (of the material) responsible for damping. There exist in a considerable amount the literature vide, Kaliski^{1,2,3}, Kaliski and Nowacki⁴, Paria⁵, Sinha^{6,7,8}, Giri^{9,10}, Dunkin and Eringen¹¹. These papers, as said above, deal with the effect of magnetic fields accommodated in purely elastic or viscoelastic materials. In keeping with this trend, the present note is concerned in general, with the problem of flexural vibrations of a viscoelastic Timoshenko rod and the equations have been illustrated by the vibration of a cantilever. It may be mentioned that this problem for the purely viscoelastic case has been considered by Mindlin¹², Mindlin and Deresiewicz¹³.

2. Fundamental Equations

Let us consider a viscoelastic rod of Voigt type of such thickness that the effects of shear and rotatory inertia can be neglected, and the problem of flexural vibrations for this type of a rod has been attempted by Lee¹⁴, Crandall and Yildiz¹⁵ in the presence of external damping. We assume that the sections of the rod remain plane after bending and we suppose that damping of the rod is also caused by the magnetic field. The magnetic field gives rise to the flux of magnetic lines of force and the motion of the beam across the flux lines causes a transverse current which, in turn, generates a retarding force. Let y and ψ be the lateral displacement and angular rotation of the cross-section at a distance x from the origin at time t . Let E be its Young's modulus, G its shear modulus, ρ its density, A the area of its cross-section, I moment of inertia about the line through the centroid perpendicular to the plane of motion, and k' is the constant depending on the cross-section. The current density vector \vec{j} is given by

$$\vec{j} = \sigma \left[\frac{\partial \vec{u}}{\partial t} \times \vec{B} \right]$$

where \vec{u} is the displacement vector, \vec{B} is the magnetic induction vector and σ is the conductivity of the rod. If there be a magnetic field of intensity H_0 in the x direction, the current density in a direction perpendicular to x is

$$R \sigma H_0 \frac{\partial y}{\partial t}$$

The total current through the element produces a retarding force per unit length. It is obtained from Biot-Savart's Law and is equal to

$$A \sigma R^2 H_0^2 \frac{\partial y}{\partial t}$$

Hence the equation for rotatory motion of an element dx of the rod is given by

$$(1) \quad \rho I \frac{\partial^2 \psi}{\partial t^2} - k' \left(\frac{\partial y}{\partial t} - \psi \right) A G - E I \frac{\partial^2 \psi}{\partial x^2} + A \sigma R^2 H_0^2 \frac{\partial \psi}{\partial t} = 0$$

and equation for transverse motion of the rod is

$$(2) \quad \rho \frac{\partial^2 y}{\partial t^2} - K G \left(\frac{\partial^2 y}{\partial x^2} - \frac{\partial \psi}{\partial x} \right) + A \sigma R^2 H_0^2 \frac{\partial \psi}{\partial t} = 0.$$

The equation satisfied by φ and ψ is

$$(3) \quad \left[\rho^2 I \frac{\partial^4}{\partial t^4} + E I K' G \frac{\partial^4}{\partial x^4} - \rho E I (1 + G K) \frac{\partial^4}{\partial x^2 \partial t^2} + A \sigma R^2 H_0^2 \rho (1 + I) \frac{\partial^3}{\partial t^3} - A \sigma R^2 H_0^2 (E I + G) \frac{\partial^3}{\partial x^2 \partial t} + K' A^2 G^2 R^2 \sigma H_0^2 \frac{\partial}{\partial t} + (A^2 \sigma^2 R^4 H_0^4 + K' G) \frac{\partial^2}{\partial t^2} \right] (\varphi, \psi) = 0$$

Equations (1), (2), (3) constitute the fundamental equations of the problem.

3. Problem of Vibration of a Cantilever

For a cantilever clamped at one end free at the other end, the clamped end being given a motion $y_0 e^{ipt}$ where y_0 is a constant, the boundary conditions are

$$(4) \quad y = y_0 e^{ipt}, \psi = 0 \text{ (at the clamped end } x = 0)$$

and

$$(7) \quad \frac{\partial y}{\partial x} - \psi = 0; \frac{\partial \psi}{\partial x} = 0$$

at the free end $x = l$.

Let us seek the solution of (3) in the form given by

$$y = y_1 e^{ipt}$$

so that, the equation giving y_1 as obtained from³, is

$$(8) \quad \left[\rho^2 I p^4 + E I K' G \frac{\partial^4}{\partial x^4} - \rho E I (1 + K G) p^2 \frac{\partial^2}{\partial x^2} + A \sigma R^2 H_0^2 \rho (1 + I) p^3 - A \sigma R^2 H_0^2 (E I + G) p \frac{\partial^2}{\partial x^2} \right.$$

$$\left. + A \sigma R^2 H_0^2 (E I + G) p^3 - A \sigma R^2 H_0^2 (E I + G) p \frac{\partial^2}{\partial x^2} \right]$$

$$+ K' A^2 G^2 R^2 \sigma H_0^2 p + (A^2 \sigma^2 R^2 H_0^4 + K' A G) p^2 \Big] y_1 = 0$$

This equation reduces to the well-known frequency equation in the absence of a magnetic field. This being a quartic in x has four roots and let its roots be m_1, m_2, m_3, m_4 . We can, therefore, write

$$(9) \quad y = e^{ipt} \left(A_1 e^{m_1 x} + A_2 e^{m_2 x} + A_3 e^{m_3 x} + A_4 e^{m_4 x} \right)$$

where A_1, A_2, A_3, A_4 are constants. We can similarly write

$$(10) \quad \psi = e^{ipt} \left(B_1 e^{m_1 x} + B_2 e^{m_2 x} + B_3 e^{m_3 x} + B_4 e^{m_4 x} \right)$$

where B_1, B_2, B_3, B_4 are constants. Further, in view of (2), the equations connecting B_r 's and A_r 's are

$$(11) \quad B_r = -\frac{1}{m_r} \left[\frac{p^2 \rho}{K' G} + m_r^2 + \frac{A R^2 \sigma^2 H_0^2 i p}{K' G} \right] A_r \\ r = 1, 2, 3, 4 \\ = -K_r A_r \text{ (say)}$$

Thus we have eight constants A_r, B_r ($r = 1, 2, 3, 4$) to be determined from eight boundary condition (6), (7), (11). These when solved give

$$A_1 = \frac{\Delta_1}{\Delta}, A_2 = \frac{\Delta_2}{\Delta}, A_3 = \frac{\Delta_3}{\Delta}, A_4 = \frac{\Delta_4}{\Delta}$$

where

$$\Delta_1 = y_0 e^{(m_2 + m_3 + m_4)l} \left[e^{-m_2 l} \left\{ k_2 k_4 m_4 (m_3 + k_3) - k_2 m_3 k_3 (m_4 + k_4) \right\} \right.$$

$$+ e^{-m_3 l} \left\{ k_3 k_2 m_2 (m_4 + k_4) - k_3 k_4 m_4 (m_2 + k_2) \right\}$$

$$\left. + e^{-m_4 l} \left\{ k_3 k_4 m_3 (m_2 + k_2) - k_2 k_4 m_2 (m_3 + k_3) \right\} \right]$$

$$\Delta_2 = -y_0 e^{(m_1 + m_3 + m_4)l} \left[k_1 e^{-m_1 l} \left\{ k_4 m_4 (m_3 + k_3) - m_3 k_3 (m_4 + k_4) \right\} \right.$$

$$+ k_3 e^{-m_3 l} \left\{ m_1 k_1 (m_4 + k_4) - m_4 k_4 (m_1 + k_1) \right\}$$

$$\left. + k_4 e^{-m_4 l} \left\{ m_3 k_3 (m_1 + k_1) - m_1 k_1 (m_3 + k_3) \right\} \right]$$

$$\Delta_3 = y_0 e^{(m_1 + m_2 + m_4)l} \left[k_1 e^{-m_1 l} \left\{ m_4 k_4 (m_2 + k_2) - m_2 k_2 (m_4 + k_4) \right\} \right.$$

$$+ k_2 e^{-m_2 l} \left\{ m_1 k_1 (m_4 + k_4) - m_4 k_4 (m_1 + k_1) \right\}$$

$$\left. + k_4 e^{-m_4 l} \left\{ m_2 k_2 (m_1 + k_1) - m_1 k_1 (m_2 + k_2) \right\} \right]$$

$$\Delta_4 = -y_0 e^{(m_1 + m_2 + m_3)l} \left[k_1 e^{-m_1 l} \left\{ m_3 k_3 (m_2 + k_2) - m_2 k_2 (m_3 + k_3) \right\} \right]$$

$$\begin{aligned}
& + k_2 e^{-m_2 l} \{ m_1 k_1 (m_3 + k_3) - m_3 k_3 (m_1 + k_1) \} \\
& + k_3 e^{-m_3 l} \{ m_2 k_2 (m_1 + k_1) - m_1 k_1 (m_2 + k_2) \} \Big] \\
\Delta = & e^{(m_2 + m_3 + m_4) l} \left\{ e^{-m_2 l} (k_2 k_4 m_3 m_4 + k_2 k_3 k_4 m_4 \right. \\
& - k_2 k_3 m_3 m_4 - k_2 k_3 k_4 m_3) + e^{-m_3 l} (k_3 k_2 m_2 m_4 \\
& + k_2 k_3 k_4 m_2 - m_2 m_4 k_3 k_4 - k_2 k_3 k_4 m_4) \\
& - e^{(m_1 + m_3 + m_4) l} \left\{ e^{-m_1 l} (k_1 k_4 m_3 m_4 + k_1 k_3 k_4 m_4 \right. \\
& \left. - k_1 k_3 m_3 m_4 - k_1 k_3 k_4 m_3) \right. \\
& + e^{-m_3 l} (k_1 k_3 m_1 m_4 + m_1 k_1 k_3 k_4 - m_1 m_4 k_3 k_4 - k_1 k_3 k_4 m_4) \\
& + e^{-m_4 l} (m_1 m_3 k_3 k_4 + k_1 k_3 k_4 m_3 - k_4 k_1 m_1 m_3 - m_1 k_1 k_3 k_4) \Big\} \\
+ & e^{(m_1 + m_2 + m_4) l} \left\{ e^{-m_1 l} (k_1 k_4 m_2 m_4 + k_1 k_2 k_4 m_4 - k_1 k_2 m_2 m_4 \right. \\
& \left. - k_1 k_2 k_4 m_2) \right. \\
& + e^{-m_2 l} (m_1 m_4 k_1 k_2 + m_1 k_1 k_2 k_4 - m_1 m_4 k_2 k_4 - k_1 k_2 k_4 m_4) \\
& + e^{-m_4 l} (m_1 m_2 k_2 k_4 + k_1 k_2 k_4 m_2 - m_1 m_2 k_1 k_4 - m_1 k_1 k_2 k_4) \Big\} \\
- & e^{(m_1 + m_2 + m_3) l} \left\{ e^{-m_1 l} (k_1 k_3 m_2 m_3 + m_3 k_1 k_2 k_3 - k_1 k_2 m_2 m_3 \right. \\
& \left. - k_1 k_2 k_3 m_2) \right. \\
& + e^{-m_1 l} (m_1 m_3 k_1 k_2 + m_1 k_1 k_2 k_3 - m_3 m_1 k_2 k_3 - m_3 k_1 k_2 k_3) \\
& + e^{-m_3 l} (m_1 m_2 k_2 k_3 + m_2 k_1 k_2 k_3 - m_1 m_2 k_1 k_3 - m_1 k_1 k_2 k_3) \Big\}
\end{aligned}$$

A_1, A_2, A_3, A_4 being known, B_1, B_2, B_3, B_4 can be obtained by using (11).

References

1. Kaliski, S. *Proc. Vibr. Probls.*, **2**, 29, 1961.
2. Kaliski, S. *Arch. Mech. Stos.*, **15**, 359, 1964.
3. Kaliski, S. Problems on Continuum Mechanics, Published by the Society of Industrial and Applied Mathematics, Pennsylvania, p. 229.
4. Kaliski, S. and Nowacki, W. *Int. Jour. Engg. Sc.*, **1**, 163, 1963.
5. Paria, G. *Proc. Camb. Phil. Soc.*, **58**, 527, 1962.
6. Sinha, D. K. *Proc. Vibr. Probls.*, **4**, 45, 1965.
7. Sinha, D. K. *Bull. Polon. Acad. des. Ses.*, **14**, 481, 1966.
8. Sinha, D. K. *Bull. Seis. Soc. Amer.*, **54**, 1777, 1964.
9. Giri, R. R. *Pure & Appld. Geophys.*, **62**, 41, 1965.
10. Giri, R. R. *Ger. Beit. Zur Geophysik.*, **75**, 391, 1966.
11. Dunkin, J. W. and Eringen, A. C. *Int. Jour. Engg. Sc.*, **1**, 461, 1963.
12. Mindlin, R. D. *Jour. Appld. Mechs.*, **18**, 31, 1955.
13. Mindlin, R. D. and Deresiewicz, H. *Proc. Ind U. S. National Congress of Applied Mechanics*, 175.
14. Lee, Ho Chang. *Jour. Appld. Mechs.*, **27**, 551, 1960.
15. Crandall, S. H. and Yildiz, Asim. *Jour. Appld. Mechs.*, **29**, 267, 1962.

The Response of Paddy to Application of Phosphates Under Varying Levels of Nitrogen

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Abstract

Field experiment was carried out to study the response of paddy to single and combined application of nitrogenous and phosphatic fertilizers. Paddy yields were enhanced by the application of nitrogen, alone or combined, with phosphates, while phosphatic fertilizers when given singly depressed the yield. In order to obtain higher returns, application of higher doses of nitrogen should be accompanied with increasing levels of phosphates.

Paddy is by far the most important and extensively grown cereal of our country. Individual responsiveness of the three most important nutrient elements, i.e., nitrogen, phosphorus and potash, have been recorded by many workers, but little information is available in literature with regard to the phenomenon of antagonism of these nutrients and precise crop response to their combined application.

Sethi (1928) reported positive response of paddy to sulphate of ammonia at Kanpur. The response of phosphates was, however, restricted only at research stations of Madhya Pradesh, Gaya in Bihar and to a lesser extent at Bombay (Sethi *et al.*, 1952). Combined application of phosphates with higher doses of nitrogen was observed to be beneficial in early plantings at Punjab (Singh, 1953). Ghose *et al.* (1956) reported that practically all types of soils responded positively to phosphatic fertilization to a varying extent. Significant increases in paddy yield were obtained with nitrogenous manuring by Relwani (1959); but when nitrogenous and phosphatic fertilizers were given together they failed to give significant yield response except in one season.

An attempt was, therefore, made in the present investigations to study the extent to which yield responses of early paddy are affected when nitrogen and phosphorus are applied jointly.

Experimental

The investigations were carried out under field conditions with N₂₂, an early variety of paddy, in light loam soils of Govt. Research Farm, Kanpur during Kharif 1964. The soil was of moderate fertility with 0.075% N, 0.0065% available P₂O₅, 0.007% available K₂O and 0.954% organic carbon. The pH of the soil was 7.7. The design of the experiment adopted was randomized block. Four levels of nitrogen, viz., 0, 22, 44, and 66 kg. N/ha. and 3 levels of phosphorus, viz., 0, 22 and 44 kg. P₂O₅/ha. were tried alone and in combination. Thus, in all there were twelve treatments, each replicated three times. The yield response of paddy to levels of phosphates, in presence and absence of varying doses of nitrogen, and also

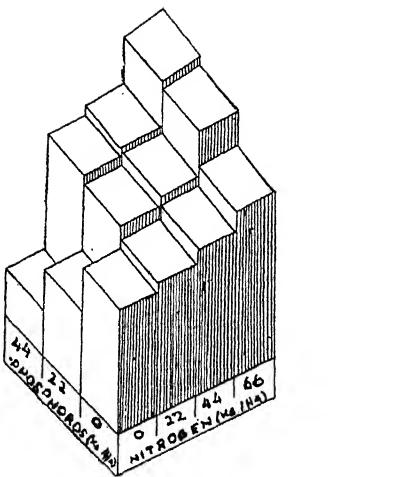


Fig. 1. Showing the effect of different levels of nitrogen and phosphorus on the yield of paddy.

the differences in the response within the treatments, have been worked out and are discussed.

Results and Discussion

The grain yield data of paddy as influenced by various levels of nitrogenous and phosphatic fertilizers are given in Table 1 (also Figure 1). Significantly higher yields were obtained by supplying nitrogenous fertilizers alone at higher levels of 44 or 66 kg. N/ha., while a slight reduction in yield was noted when phosphatic fertilizers were used singly. However, grain production was considerably augmented by phosphates when applied in combination with nitrogenous fertilizers. Highest paddy yield was recorded in the treatment where 66 kg. N combined with 44 kg. P_2O_5 /ha. was applied.

TABLE 1

Grain yield of paddy in Qnt./ha. as affected by various levels of nitrogenous and phosphatic fertilizers

Treatments (Kg./ha.)	N ₀	N ₂₂	N ₄₄	N ₆₆
P ₀	12.46	13.15	15.39	17.57
P ₂₂	12.33	14.51	17.10	18.87
P ₄₄	12.26	15.05	17.37	19.62
C. D. for N	2.07			

The average response of paddy to the twelve treatment combination of nitrogenous and phosphatic dressings are shown in Table 2. Application of phosphate in the absence of nitrogen produced a negative response at either of its levels. But, enhanced response at lower levels of phosphates was noticed when applied together with nitrogenous fertilizers upto a dose of 44 kg. N/ha.,

TABLE 2

Response of paddy to phosphate in presence and absence of nitrogen (Qnt./ha.)

Response to 22 kg. P ₂ O ₅ /ha. (P ₂₂)	Response to 44 kg. P ₂ O ₅ /ha. (P ₄₄)
1. Response to 22 kg. P ₂ O ₅ (P ₂₂) in presence of N ₀ (N ₀ P ₂₂ - N ₀ P ₀) - 0·13	11. Response to 44 kg. P ₂ O ₅ (P ₄₄) in presence of N ₀ (N ₀ P ₄₄ - N ₀ P ₀) - 0·20
2. Response of 22 kg. P ₂ O ₅ (P ₂₂) in the presence of 22 kg. N (N ₂₂) (N ₂₂ P ₂₂ - N ₂₂ P ₀) 1·36	12. Response to 44 kg. P ₂ O ₅ (P ₄₄) in presence of 22 kg. N (N ₂₂) (N ₂₂ P ₄₄ - N ₂₂ P ₀) 1·90
3. Response of 22 kg. P ₂ O ₅ (P ₂₂) in the presence of 44 kg. N(N ₄₄) (N ₄₄ P ₂₂ - N ₄₄ P ₀) 1·71	13. Response to 44 kg. P ₂ O ₅ (P ₄₄) in presence of 44 kg. N (N ₄₄) (N ₄₄ P ₄₄ - N ₄₄ P ₀) 1·98
4. Response of 22 kg. P ₂ O ₅ (P ₂₂) in the presence of 66 kg. N(N ₆₆) (N ₆₆ P ₂₂ - N ₆₆ P ₀) 1·30	14. Reponse to 44 kg. P ₂ O ₅ (P ₄₄) in presence of 66 kg. (N ₆₆) (N ₆₆ P ₄₄ - N ₆₆ P ₀) 2·05
5. Difference of response to 22 kg. P ₂ O ₅ at 22 kg. N vs. ON (N ₂₂ P ₂₂ - N ₂₂ P ₀) - (N ₀ P ₂₂ - N ₀ P ₀) 1·49	15. Difference of response to 44 kg. P ₂ O ₅ at 22 kg. N vs. ON (N ₂₂ P ₄₄ - N ₂₂ P ₀) - (N ₀ P ₄₄ - N ₀ P ₀) 2·10
6. Difference of response to 22 kg. P ₂ O ₅ at 44 kg. N vs. 22 kg. N(N ₄₄ P ₂₂ - N ₄₄ P ₀) - (N ₂₂ P ₂₂ - N ₂₂ P ₀) 0·35	16. Difference of response to 44 kg. P ₂ O ₅ at 44 kg. N vs. 22 kg. N (N ₄₄ P ₄₄ - N ₄₄ P ₀) - (N ₂₂ P ₄₄ - N ₂₂ P ₀) 0·08
7. Difference of response to 22 kg. P ₂ O ₅ at 44 kg. N vs. ON (N ₄₄ P ₂₂ - N ₄₄ P ₀) - (N ₀ P ₂₂ - N ₀ P ₀) 1·84	17. Difference of response to 44 kg. P ₂ O ₅ at 44 kg. N vs. ON (N ₄₄ P ₄₄ - N ₄₄ P ₀) - (N ₀ P ₄₄ - N ₀ P ₀) 2·18
8. Difference of response to 22 kg. P ₂ O ₅ at 66 kg. N vs. ON (N ₆₆ P ₂₂ - N ₆₆ P ₀) - (N ₀ P ₂₂ N ₀ P ₀) 1·43	18. Difference of response to 44 kg. P ₂ O ₅ at 66 kg. N vs. ON (N ₆₆ P ₄₄ - N ₆₆ P ₀) - (N ₀ P ₄₄ - N ₀ P ₀) 2·25
9. Difference of response to 22 kg. P ₂ O ₅ at 66 kg. N vs. 22 kg. N (N ₆₆ P ₂₂ - N ₆₆ P ₀) - (N ₂₂ P ₂₂ - N ₂₂ P ₀) - 0·06	19. Difference of response to 44 kg. P ₂ O ₅ at 66 kg. N vs. 22 kg. N (N ₆₆ P ₄₄ - N ₆₆ P ₀) - (N ₂₂ P ₄₄ - N ₂₂ P ₀) 0·15
10. Difference of response to 22 kg. P ₂ O ₅ at 66 kg. N vs. 44 kg. N (N ₆₆ P ₂₂ - N ₆₆ P ₀) - (N ₄₄ P ₂₂ - N ₄₄ P ₀) - 0·41	20. Difference of response to 44 kg. P ₂ O ₅ at 66 kg. N vs. 44 kg. N (N ₆₆ P ₄₄ - N ₆₆ P ₀) - (N ₄₄ P ₄₄ - N ₄₄ P ₀) 0·07

The differences in the response of 22 kg. P_2O_5 /ha. alone and in combination with 22 kg. N/ha. was 1.49 Qnt./ha. The highest difference in response to 22 kg. P_2O_5 was observed in the presence of 44 kg. N and 22 kg. P_2O_5 without nitrogen, i.e., 1.84 Qnt./ha., the difference in response to 22 kg. P_2O_5 with 44 kg. N and 22 kg. $P_2O_5 + 22$ kg. N was 0.35 Qnt./ha. This treatment proved to be superior when compared even with the differences in response to 22 kg. P_2O_5 with 66 kg. N and 22 kg. P_2O_5 used either with 22 or 44 kg. N/ha. which were negative.

A continued increase in the response of higher doses of phosphates, i.e., 44 kg. P_2O_5 /ha. was observed with increasing levels of nitrogenous fertilizers from 22 to 66 kg. N/ha. From a comparison of the differences in response of phosphate (44 kg. P_2O_5 /ha.), in presence or absence of various levels of nitrogen, it could be inferred that unlike lower levels of phosphates, the highest difference in response (2.25 Qnt./ha.) was noticed with 66 kg. N + 44 kg. P_2O_5 and 44 kg. P_2O_5 alone. This was closely followed by the difference in response to 44 kg. P_2O_5 with 44 kg. N and 44 kg. P_2O_5 without nitrogen.

The observation that phosphates alone gave a depressive effect on the yield of paddy grain is in conformity with the findings of Mann and Purnapragnachar (1963) and Mehrotra *et al* (1967). The two-fold action of nitrogen upon the phosphorus availability, viz., the solvent action upon the phosphatic fertilizers resulting from the process of nitrification of ammonium sulphate (Shrikhande and Yadava, 1954) and increased uptake of phosphorus through a deeper and more extensive root system (Grunes, 1959) might have been the reasons for increased yield obtained through combined fertilization of nitrogen and phosphates.

Reduced response observed in case of 22 kg. P_2O_5 , when given in combination with 66 kg. N/ha. may be due to unbalanced fertilization caused by limited supply of phosphorus which when increased to 44 kg. P_2O_5 responded positively.

References

1. Ghosh, R. L. M., Ghatge, M. B. and Subramanyan, V. *Rice in India* I. C. A. R. New Delhi, 1956.
2. Grunes, D. L. Effect of nitrogen on the availability of soil and Fertilizer phosphorus to plants. *Adv. Agron.*, 2, 369-396, 1959.
3. Mann, H. S. and Purnapragnachar, H. Further inferences from the data on response of wheat and paddy to phosphate as affected by nitrogen. *Ind. J. Agron.*, 8, 384-392, 1963.
4. Mehrotra, O. N., Sinha, N. S. and Srivastava, R. D. L. The uptake of nitrogen by wheat plant at various stages of growth as influenced by phosphorus. *Plant and Soil.*, 26, 361-368, 1967.
5. Relwani, L. L. Response of rice varieties to different levels of nitrogen and phosphate. *Ind. J. Agron.*, 4, 8-17, 1959.
6. Sethi, R. L. Preliminary note on rice crop in U. P. *Imperial Agric. Res. Inst. Bull.* 186, 1928.
7. Sethi, R. L., Ramiah, K. and Abraham, T. P. *Manuring of rice in India*. (Revised) I. C. A. R., Misc. Bull., 38, 1952.
8. Shrikhande, J. G. and Yadav, J. S. P. Effect of N upon availability of P. *J. Ind. Soc. Soil. Sci.*, 2, 115, 1954.
9. Singh, G. Rice in various states. *Rice News Teller.*, 1, 38, 1953.

Kinetics and Mechanism of the Silver (I) catalysed Oxidation of Thallium (I) by Peroxydisulphate

By

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Summary

In the present communication the silver (I) catalysed oxidation of thallium (I) to thallium (III) by peroxydisulphate has been studied kinetically from the mechanistic point of view. The reaction has been found to be of first order with respect to peroxydisulphate and silver (I), but independent of the concentration of thallium (I). It is postulated that the reaction proceeds by propagation of a chain initiated by the decomposition of peroxydisulphate by silver (I) to give sulphate free radical and higher-valent silver (II). The formation of bivalent silver has been emphasised and the chain also involves thallium (II) as an intermediate product.

Introduction

The oxidation of several organic compounds and inorganic ions has been reported by peroxydisulphate ion¹. The silver (I) catalysed oxidations by peroxydisulphate have been usually found to possess unit order with respect to the catalyst. In certain cases colloidal silver has also been utilised to catalyse the oxidations by peroxydisulphate².

By oxidising agents thallium (I) is transformed into thallium (III). Carpenter and coworkers³ have studied the thallous-thallic exchange in systems containing bromide and also studied the oxidation of thallium (I) by bromine. The potentiometric titrations of thallium (I) by potassium iodate in 6-9N HCl were carried out by Alimarin and coworkers⁴. Issa and Allam⁵ investigated the oxidation of thallium (I) with alkaline potassium manganate (IV) and observed that the reaction is accelerated by adding sodium chloride.

In the present investigation potassium peroxydisulphate has been used as an oxidising agent with a view to study the kinetics and mechanism of the silver (I) catalysed reaction. The reaction is slow in the absence of the catalyst at 25°C but proceeds with a measurable rate at higher temperatures⁶. In presence of silver (I) the reaction is, however, accelerated to great extent and therefore the kinetic data of the silver (I) catalysed oxidation of thallium (I) is recorded here in this paper.

Experimental

Aqueous solutions of potassium peroxydisulphate were always freshly prepared just before starting of an experiment from a sample of E. Merck, Proanalysi and stored in Jena glass vessel. Thallium (I) was prepared by

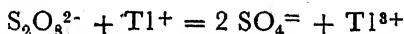
dissolving the AnalaR sample of thallous sulphate in bidistilled water and its strength was checked by usual methods. The stock solution of silver nitrate was prepared by dissolving AnalaR (BDH) sample of the reagent in double-distilled water and was stored in dark bottles.

Calculated quantities of the solution of thallous sulphate with requisite amount of redistilled water, was taken in the Jena glass reaction bottle and was placed in a water thermostat maintained at the desired temperature. Peroxydisulphate solution and silver nitrate solution were placed separately in the same bath. The reaction was started by transferring the calculated quantities of silver nitrate and peroxydisulphate in the reaction vessel.

To study the progress of the reaction, aliquot portions of the reaction mixture were withdrawn at definite intervals of time and were titrated iodometrically for thallium(1)⁷ wherefrom the amounts of peroxydisulphate consumed were calculated.

Results

Stoichiometry: To verify the stoichiometry of the reaction a solution containing $6 \cdot 0 \times 10^{-2}$ M $\text{K}_2\text{S}_2\text{O}_8$, $1 \cdot 0 \times 10^{-2}$ M Tl_2SO_4 and $5 \cdot 0 \times 10^{-4}$ M AgNO_3 was allowed to react for twenty four hours. On estimation it was found that the decrease in Tl_2SO_4 concentration was identical with that in $\text{S}_2\text{O}_8^{2-}$ in accordance with the equation



Peroxydisulphate dependence: To determine the order of the reaction with respect to the oxidant, first order rate constants have been calculated with respect to peroxydisulphate with the progress of time at three different concentrations of the oxidant, keeping other factors the same. The data are represented in the following table :

TABLE 1

	$\text{Tl}_2\text{SO}_4 - 0 \cdot 005 \text{ M}$	$\text{AgNO}_3 - 0 \cdot 001 \text{ M}$	Temperature 45°C
Time in minutes	$\text{K}_2\text{S}_2\text{O}_8 : 0 \cdot 10 \text{ M}$	$\text{K}_2\text{S}_2\text{O}_8 : 0 \cdot 08 \text{ M}$	$\text{K}_2\text{S}_2\text{O}_8 : 0 \cdot 06 \text{ M}$
	$k/2 \cdot 303 \times 10^5$ min^{-1}	$k/2 \cdot 303 \times 10^5$ min^{-1}	$k/2 \cdot 303 \times 10^5$ min^{-1}
6	-	-	-
12	30.50	36.83	36.66
18	29.25	35.66	37.91
24	29.33	35.44	36.68
30	29.37	35.83	37.50
36	30.33	35.76	36.96
42	30.77	35.19	37.06
48	30.83	35.08	36.80
54	31.83	35.26	37.28
60	30.80	35.16	37.39
Average	30.20	35.57	37.03
or $k =$	$7 \cdot 00 \times 10^{-4} \text{ min}^{-1}$	$8 \cdot 10 \times 10^{-4} \text{ min}^{-1}$	$8 \cdot 50 \times 10^{-4} \text{ min}^{-1}$

It is clear from the above table that first order rate constants with respect to peroxydisulphate have fairly agreeable values showing the reaction to be of first order in peroxydisulphate. However, an increase in peroxydisulphate concentration results in slight decrease in first order rate constants. This inhibitory effect is due to the specific action of K^+ ions as reported by Agrawal and Mushran⁸ during the study of the oxidation of urea and acetamide by peroxydisulphate.

Thallium (I) dependence :

In order to evaluate the order of the reaction with respect to thallium (I), the reaction was studied at four different initial concentrations of thallous sulphate. The average values of first order rate constants are summarised in the following table :

TABLE II
 $K_2S_2O_8 - 0.10\text{ M}$, $AgNO_2 - 0.001\text{ M}$, Temperature $45^\circ C$

Initial concentration of thallium (I) sulphate M	Values of rate constants $k \times 10^4 \text{ min}^{-1}$
0.0050	7.0
0.0075	8.0
0.0100	7.5
0.0125	7.7

It can well be inferred from the above table that the concentration of thallium (I) has a little or no effect on the first order rate constants and the reaction is thus independent of the concentration of the reducing substrate.

Silver Nitrate dependence

To determine the order of the reaction with respect to the catalyst, silver nitrate concentration was varied from $2.5 \times 10^{-4}\text{ M}$ to $10.0 \times 10^{-4}\text{ M}$ keeping the concentrations of the other reactants constant. It has been found that the rate constants vary linearly with silver (I) concentrations (Fig. 1) and the plots of $\log k$ against $\log [Ag(1)]$ (Fig. 2) yield straight lines with unit slope, showing the direct dependence of rate on silver (I) concentrations.

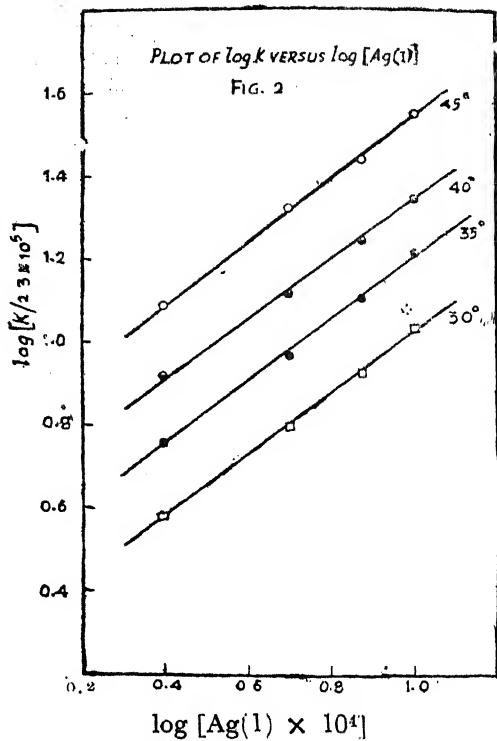
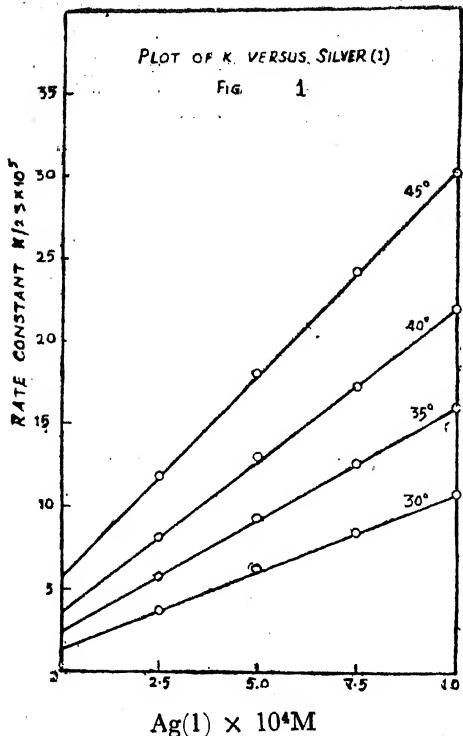
Temperature dependence

The kinetic investigations were also carried out at different temperatures to obtain some important thermodynamical parameters. Taking the reaction concentrations as $K_2S_2O_8 - 0.10\text{ M}$, $Tl_2SO_4 - 0.005\text{ M}$ and $AgNO_3 - 0.001\text{ M}$ the magnitudes of the energy of activation, entropy of activation and frequency factor have been calculated as 13.56 K. cals , -26.10 E. U. and $2.21 \times 10^7\text{ l. mole}^{-1}\text{ sec}^{-1}$ respectively.

Discussion

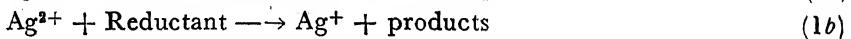
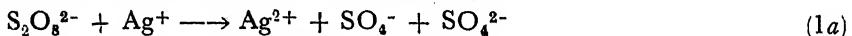
The observed rate law for the silver (I) catalysed oxidations by peroxydisulphate is usually expressed as¹ :

$$-\frac{d}{dt} (S_2O_8^{2-}) = k [S_2O_8^{2-}] [Ag^+]$$

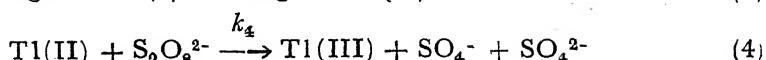
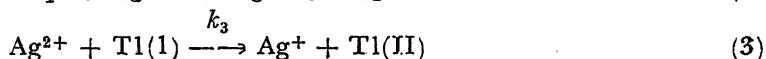
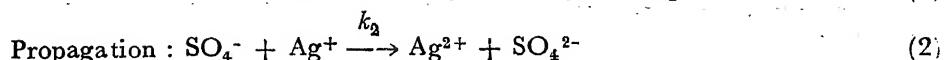
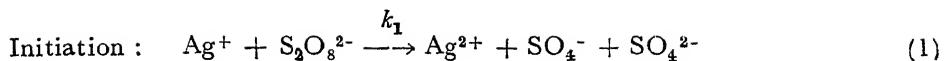


The rate at any instant being proportional to the peroxydisulphate and (constant) silver (I) concentration. The reaction is essentially bimolecular, although the data for any given concentration of the catalyst confirm to a unimolecular rate law.

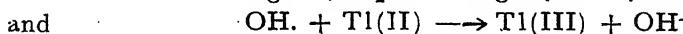
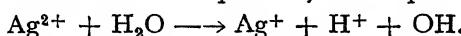
During the oxidation by peroxydisulphate, catalysed by silver (I), single electron transference is suggested which is in accordance with the observations of Higginson and Marshall⁹ and is supported by the study of the reaction between peroxydisulphate and hydrogen peroxide catalysed by both silver (I) and bisdipyridyl silver (I). In this way the generally accepted mechanism of the silver (I) catalysed reactions is given by the following steps:



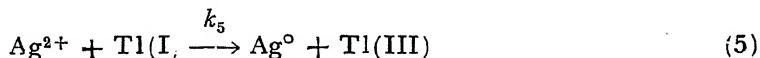
The oxidation of thallium (I) by peroxydisulphate catalysed by silver (I) involves an overall two electron transfer and a chain reaction sets in. The proposed chain mechanism, which is supported by the experimental data, is initiated by the decomposition of the oxidant by silver (I) which gives SO_4^- free radical and the higher valent silver (II). The SO_4^- formed reacts with more of silver (I) to give silver (II) which in turn oxidises thallium (I) to thallium (II), an unstable intermediate, which readily combines with peroxydisulphate to yield the product and a SO_4^- free radical and the chain continues. The chain process may be represented by a series of reactions as follows :



If the termination of the chain takes place by the steps



it can be shown that the reaction would not be independent of the substrate concentration. The termination would, therefore, occur by the process :



The formation of silver metal is experimentally supported by the appearance of black particles when the reactants are kept for sufficiently long time. The step (5) may, however, consist of several more steps.

Several differential equations can be set up from the above scheme :

$$-\frac{d}{dt} (\text{S}_2\text{O}_8^{2-}) = k_1 [\text{S}_2\text{O}_8^{2-}] [\text{Ag}^+] + k_4 [\text{Tl(II)}] [\text{S}_2\text{O}_8^{2-}] \\ = \{k_1[\text{Ag}^+] + k_4[\text{Tl(II)}]\} [\text{S}_2\text{O}_8^{2-}] \quad (6)$$

$$\frac{d}{dt} (\text{Ag}^{2+}) = k_1 [\text{Ag}^+] [\text{S}_2\text{O}_8^{2-}] + k_2 [\text{Ag}^+] [\text{SO}_4^-] \\ - k_3 [\text{Ag}^{2+}] [\text{Tl(I)}] - k_5 [\text{Ag}^{2+}] [\text{Tl(I)}] \quad (7)$$

$$\frac{d}{dt} (\text{SO}_4^-) = k_1 [\text{Ag}^+] [\text{S}_2\text{O}_8^{2-}] - k_2 [\text{SO}_4^-] [\text{Ag}^+] \\ + k_4 [\text{Tl(II)}] [\text{S}_2\text{O}_8^{2-}] \quad (8)$$

$$\frac{d}{dt} (\text{Tl(II)}) = k_3 [\text{Ag}^{2+}] [\text{Tl(I)}] - k_4 [\text{Tl(II)}] [\text{S}_2\text{O}_8^{2-}] \quad (9)$$

By the steady state hypothesis,

$$\frac{d}{dt} (\text{Ag}^{2+}) = \frac{d}{dt} (\text{SO}_4^-) = \frac{d}{dt} (\text{Tl(II)}) = 0 \quad (10)$$

Making use of relations (7), (8), (9) and (10) the equation (6) may be simplified to give the following rate law :

$$-\frac{d}{dt} (\text{S}_2\text{O}_8^{2-}) = \frac{k_1 k_3}{k_5} [\text{S}_2\text{O}_8^{2-}] [\text{Ag}^+] \quad (11)$$

From the above rate law the silver (I) catalysed oxidation of thallium (I) by peroxydisulphate would be of first order with respect to peroxydisulphate and silver (I) and of zero order with respect to thallium (I), which is in complete accordance with the experimental observations.

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References

1. House, D. A. *Chem. Revs.*, **62**, 185, 1962.
2. Singh, V. and Mushran, S. P. *Indian J. Chem.*, **3**, 551, 1965.
3. Carpenter, L. G. and coworkers. *Disc. Farad Soc.*, **29**, 92, 1962.
4. Alimarin, I. P., Tseng, Y. A. and Puzdrenkova, I. V. *Vestnik Morkov Univ.*, **13**, 201, 1958.
5. Issa, I. M. and Allam, M. G. E. *Z. anal. Chem.*, **168**, 83, 1959.
6. Shinghal, R. K., Agrawal, M. C. and Mushran, S. P. *Z. Physik. Chem. (Frankfurt)*, **60**, 34, 1968.
7. Vogel, A. I. A Text-Book of Quantitative Inorganic Analysis. *Longmans* 1961.
8. Agrawal, M. C. and Mushran, S. P. *J. Indian Chem. Soc.*, **42**, 629, 1965 ; **43**, 343, 1966.
9. Higginson, W. C. and Marshall, J. W. *J. Chem. Soc.*, 447, 1957.

A method of inclusion of zero-point energy in the Potential parameters of inert Gas-solids

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Abstract

The paper describes a method of inclusion of zero-point energy in the parameters A, B and ρ of the potential

$$\phi(r) = -Ar^{-6} + AB \exp(-r/\rho),$$

for solid helium, neon, argon, krypton and xenon. The equilibrium conditions and experimental crystal properties at absolute zero are used for this purpose. Evaluation of these parameters requires the knowledge of the vibration spectrum of the crystal which is itself a function of all these. An iterative process is therefore used for the evaluation by estimating the static lattice energy through successive approximations. The effect of zero-point energy over the parameters is studied by comparing their values with those calculated without it. The heat capacities and other thermodynamic properties calculated with these parameters show a fair agreement with recent experimental data.

1. Introduction

Among molecular solids, the solidified inert gases are particularly interesting due to a number of reasons¹. The most interesting feature of this simple class of solids is the relatively high zero-point energy which they possess. The zero-point energy increases the lattice constant, decreases the cohesive energy and gives rise to anharmonicity of lattice vibrations even at lowest temperatures. The effects are most marked in case of helium, but become less appreciable as one passes to the other members of the group with higher atomic numbers.

The effect of zero-point energy on the bulk properties is measurable at all temperatures, although it is more predominant at lower ones. This has been studied by Salter², who showed that it gives rise to Cauchy-discrepancy ($C_{12} \neq C_{44}$) in inert gas-crystals. Other thermodynamic properties have been studied by Domb and Zucker³, Zucker⁴, Henkel⁵ and Horton and Leech⁶, etc., who obtained satisfactory agreement with experimental results using Lennard-Jones potential $\phi(r) = -ar^{-6} + br^{-m}$. Guggenheim as McGlashan's⁷ and Horton and Leech's calculations show that Lennard-Jones potential is inadequate⁸ to account for the thermal properties of these solids even after incorporating the zero-point quantum effects.

Herzfeld and Mayer⁹ and Kane¹⁰ have studied melting and other thermal properties of these solids by using another potential $\phi(r) = -Ar^{-6} + AB \exp(-r/\rho)$, with a more acceptable exponential repulsive term ($AB \exp(-r/\rho)$) in place of br^{-m} , in the Lennard-Jones potential. The results obtained by these workers were not satisfactory. This may be due to the fact that they used two values⁹ for the parameter ρ ,

namely $\rho = 0.345 \text{ \AA}^\circ$ and 0.2091 \AA° , and calculated the other two (A and B) using sublimation energy and lattice constant at 0°K . The present authors aimed at calculating the three parameters A , B and ρ of the potential (1), separately for each gas-solid by including zero-point energy and to recalculate the thermodynamic properties using these parameter. The present paper describes only the method by which zero-point energy has been included in the potential parameters. The two sets of parameters, with and without zero-point energy, are found to differ appreciably.

2. Determination of Potential Parameters

We have chosen the following interatomic potential $\phi(r)$ for a pair of atoms of the inert gas-solids separated by a distance r .

$$\phi(r) = -Ar^{-6} + AB \exp(-r/\rho), \quad (1)$$

where A , B and ρ are constants. The inverse sixth power term represents the van der Waals attraction due to dipole-dipole interaction and the exponential term stands for overlap repulsion due to Pauli's exclusion principle. The two forces are characteristic of neutral and isotropic atoms and may be regarded as central, two-body forces of short range. Unlike Herzfeld and Mayer⁹ and Kane¹⁰ we have taken ρ as an undetermined parameter. The three parameters are determined as follows.

2.1 Equilibrium conditions.—The parameters A , B and ρ can be determined from the following equilibrium conditions of the lattice. The conditions assume their simplest form at absolute zero of temperature and can be written as

$$F = -L, \quad (2)$$

$$P = - \left(\frac{\partial F}{\partial V} \right) = 0, \quad (3)$$

$$\beta = \left(V \frac{\partial P}{\partial V} \right)^{-1} = \frac{1}{V} \left(\frac{\partial^2 F}{\partial V^2} \right)^{-1}, \quad (4)$$

where $V = Nr^3/\sqrt{2}$ is the molar volume, F the Helmholtz free energy and L , P and β are respectively the sublimation energy, pressure and isothermal compressibility of the crystal.

2.2 Helmholtz Free Energy.—According to statistical mechanics the free energy F of a system is related to its all possible energy levels through the partition function Z , as

$$F = -kT \log Z, \quad (5)$$

where k is Boltzmann constant. The total eigen value E_n of the energy operator is the sum of static lattice energy E_{st} and the vibrational energy, that is

$$E_n = E_{st} + \sum_n \sum_i \sum_K (\frac{1}{2} + n) \hbar v(i, K). \quad (6)$$

The summation is carried over all the wave vectors K ($|K| = \lambda^{-1}$) and for all eigen values of an oscillator. For a cubic crystal having one particle per unit cell i runs from 1 to 3. So the partition function

$$Z = \sum \exp(-E_n/kT), \\ = \exp(-E_{st}/kT) \sum_{i,K} \frac{\exp[-\frac{1}{2} \hbar v(i, K)/kT]}{1 - \exp[-\hbar v(i, K)/kT]} \quad (7)$$

Now combining (5) and (7), we obtain

$$F = E_{st} + \sum_i \sum_K 2 kT \operatorname{Sinh} \frac{\hbar v(i, K)}{2kT}. \quad (8)$$

The free energy per mole of an inert gas crystal may be obtained by carrying out the summation over N (Avogadro number) states of vibration K and over i (1, 2, 3).

2.3 Static Lattice Energy. The static lattice energy E_{st} is just the lattice potential energy and is the sum of potential energy of all the pairs formed by one atom with all the other atoms at distance r from it. If there are N atoms in the crystal, the static lattice energy can be expressed as

$$E_{st} = \frac{1}{2} N \sum \phi(r). \quad (9)$$

The factor $\frac{1}{2}$ allows for the fact that the summation process counts every atom twice.

For an inert gas crystal, the static lattice energy is written as

$$E_{st} = \frac{1}{2} N [- S_1 A r_0^{-6} + S_2 A B \exp(-r_0/\rho)], \quad (10)$$

where r_0 is the nearest neighbour distance at $0^\circ K$. S_1 and S_2 are constants which depend upon the nature of the lattice. For face-centred cubic lattice S_1 has been evaluated to be 14.4539 by Jones and Ingham¹¹. For the same f.c.c. lattice the constant S_2 may be defined as

$$S_2 = \sum M_m \exp[-r_0(\sqrt{m}-1)/\rho], \quad (11)$$

where M_m stands for the number of m th neighbours and the summation is carried out over the entire crystal. The series has been evaluated as 12.04568 by us using a method of successive approximations.

Now for convenience we define the new variables

$$\Phi = \sum \phi(r), \quad \Phi' = \frac{1}{r} \left(\frac{\partial \Phi}{\partial r} \right) \text{ and } \Phi'' = \frac{\partial^2 \Phi}{\partial r^2}, \quad (12)$$

where r is the interatomic distance. On substituting the value of F from (8), the conditions of equilibrium (2), (3) and (4) may be rewritten in terms of the above variables, at absolute zero of temperature, as

$$\frac{1}{2} N \Phi_0 + \sum_i \sum_K [\frac{1}{2} \hbar v(i, K)]_0 = -L_0, \quad (13)$$

$$\frac{r_0^{-1}}{\omega \sqrt{2}} \Phi'_0 + \frac{h}{2} \sum_i \sum_K \left[\frac{\partial v(i, K)}{\partial V} \right]_0 = 0, \quad (14)$$

$$\text{and } \frac{r_0^{-1}}{9\sqrt{2}} (\Phi''_0 - 2\Phi'_0) + \frac{N h r_0^3}{2\sqrt{2}} \sum_i \sum_K \left[\frac{\partial^2 v(i, K)}{\partial V^2} \right]_0 = \frac{1}{\beta_0} \quad (15)$$

where the suffix 0 indicate the values of the variables of absolute zero of temperature. The frequency dependent terms in (13), (14) and (15) represent the effect of zero-point energy (E_z) and are by no means insignificant in the present case. The second term in (13) is E_z itself. These equations cannot be solved directly for the determination of Φ'_0 and Φ''_0 , and hence of the parameters A , B and ρ , since the evaluation of frequency dependent terms requires the knowledge of the

vibration spectrum which itself is a function of the parameters. Therefore they have been estimated by the Debye theory of specific heats. Representing the frequency dependent terms in (14) and (15) by X and Y respectively, we have

$$E_z = \frac{9}{8} R \theta_0, X = \frac{-9}{4\sqrt{2}} \frac{k \theta_0}{r_0^3} \gamma_0 \text{ and } Y = |X|(1 + \gamma_0); \quad (16)$$

where γ_0 and θ_0 are respectively the Grüneisen constant and Debye characteristic temperature at $0^\circ K$ and R is the gas constant.

TABLE I
Experimental values of constants used

Solid	$a_0 \times 10^8 \text{ cm}$	$\beta_0 \times 10^{11} \text{ cm}^2 \text{ dyne}^{-1}$:	$L_0 \text{ Cal mole}^{-1}$	$E_z \text{ Cal mole}^{-1}$	$\theta_0 \text{ }^\circ K$	γ_0
*He	5.198 D	235.70 D	12 D	47 C	20.00 D	2.60 E
Ne	4.462 P	10.00 P	448 P	154 P	66.60 P	3.22 H
Ar	5.312 P	9.98 P	1846 P	187 P	83.66 C	2.77 H
Kr	5.644 P	3.99 P	2666 P	145 P	64.87 C	2.51 H
Xe	6.131 P	2.80 P	3828 P	123 P	55.00 P	2.87 H

*Solid at 25 atm pressure and $0^\circ K$.

P - Pollack¹², H - Horton *et al*⁶

C - Calculated by $E_z = 9R \theta_0/8$, using Morrison and coworker's^{20,21} values of E_z .

D - Dugdale and Simon¹⁸, E - Edwards and Pandorf¹⁹.

Now replacing the frequency dependent terms in (13), (14) and (15) by E_z , X and Y , and solving the equations we get,

$$A = a - \frac{r_0^9 [3 \rho Y + (2 \rho + r_0) X]}{\sqrt{2} S_1 (r_0 - 7\rho)}, \quad (17)$$

$$B = b + \frac{3\sqrt{2} X \rho r_0^2}{S_2 A} \exp(r_0/\rho), \quad (18)$$

$$\rho = r_0 \left[\log S_2 B - \log \left\{ \frac{S_1}{r_0^6} - \frac{2(L_0 + E_z)}{NA} \right\} \right]^{-1}, \quad (19)$$

$$\text{where } a = \frac{3r_0^9 \rho}{\sqrt{2} S_1 (r_0 - 7\rho) \beta_0}, \quad b = \frac{6S_1 \rho}{S_2 r_0^7} \exp(r_0/\rho) \text{ and } r_0 = a_0/\sqrt{2} \quad (20)$$

The expressions for A and B contain ρ and that of ρ contains A and B explicitly, therefore they cannot be evaluated independently. An iterative method has been applied to obtain the values of the parameters A , B and ρ .

3. Computation and Discussion

In order to obtain self consistent values of A , B and ρ , first X and Y are put equal to zero in (17) and (18) and an approximate value of ρ is obtained by replacing A and B by a and b in (13). With this value of ρ approximate values of A and

B are found out, which on being substituted in (19) give next approximate value of ρ . The self consistent values of the parameters for He, Ne, Ar, Kr and Xe are calculated by a number of iterations, using IBM-1620 Digital Computer. We have also determined these parameters without incorporating E_z . The two sets of A , B and ρ are given in Table 2.

TABLE 2
Values of parameters A , B and ρ .

Solid	With E_z			Without E_z		
	$A \times 10^{58}$ cm^{-6}	$B \times 10^{-48}$ cm^{-6}	$\rho \times 10^8 \text{ cm}$	$A \times 10^{58}$ cm^{-6}	$B \times 10^{-48}$ cm^{-6}	$\rho \times 10^8 \text{ cm}$
*He	0.04468	1.37332	0.44174	0.04521	1.98937	0.42317
Ne	0.13388	18.24467	0.31019	0.13590	21.96870	0.30495
Ar	1.13529	32.64233	0.31553	1.09763	34.78721	0.31300
Kr	2.42587	10.12222	0.36167	2.38158	10.42538	0.36021
Xe	4.71992	39.19334	0.33218	4.65544	40.15069	0.33116

The two sets of parameters on being compared show that zero-point energy increases ρ and decreases B in all the cases. But the parameter A increases in case of heavy rare gas solids (argon, krypton and xenon) and decreases in case of helium and neon. The heat capacities, thermal expansion and isothermal compressibilities of argon, krypton and xenon calculated with these parameters, which have been corrected for zero-point energy, are in fair agreement with recent experimental data^{13, 14, 15, 16}. However, the discrepancy between calculated and observed results of these thermodynamic properties in case of neon and helium is large^{14, 16, 17}.

It is well-known that the interaction in the case of helium is of different type and quantum effects are predominant. Neon being close the helium in the periodic table, must share some of its characteristics¹⁴. The anomaly may, therefore, be viewed in this light..

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References

1. Dobbs, E. R. and Jones, G. O. *Rep. Progr. Phys.* **20**, 516, 1957.
2. Salter, L. *Phil. Mag.* **45**, 360, 1954a, 369, 1954b
3. Domb, C. and Zucker, I. J. *Nature*, **178**, 484, 1956.
4. Zucker, I. J. *Phil. Mag.*, **3**, 987, 1958.
5. Henkel, J. H. *Chem. Phys.* **23**, 681, 1955.
6. Horton, G. K. and Leech, J. W. *Proc. Phys. Soc.*, **82**, 816, 1963.
7. Guggenheim, E. A. and McGlashan, M. L. *Proc. Roy. Soc.*, **A225**, 456, 1960.

*At 25 atm. pressure and 20.18 cm³ molar volume.

8. Boato, G. *Cryogenics*, **4(2)**, 65, 1964.
9. Herzfeld K. F. and Mayer, M. G. *Phys. Rev.* **46**, 995, 1934.
10. Kane, B. G. *J. Chem. Phys.* **7**, 603, 1939.
11. Jones, E. and Ingham, A. E. *Proc. Roy. Soc.*, **A107**, 636, 1925.
12. Pollack, G. L. *Rev. Mod. Phys.* **36(3)**, 748, 1964.
13. Gupta, N. P. and Dayal, B. *Phys. Stat. Sol.*, **15**, 465, 1966.
14. Gupta, N. P. and Dayal, B. *Phys. Stat. Sol.*, **18**, 731, 1966.
15. Gupta, N. P. and Dayal, B. *Phys. Stat. Sol.*, **20**, 1967.
16. Gupta, N. P. and Dayal, B. *Phys. Stat. Sol.*, (communicated)
17. Gupta, N. P. and Dayal, B., (unpublished).
18. Dugdale, J. S. and Simon, F. *Proc. Roy. Soc.*, **A218**, 291, 1953.
19. Edward, D. O. and Pandorf, R. C. *Phys. Rev.*, **140**, 816, 1965.
20. Flubacher, P., Leadbetter, A. J. and Morrison J. A. *Proc. Phys. Soc.*, **38**, 1449, 1961.
21. Beaumont, R. H., Chihara, H. and Morrison, J. A. *Proc. Phys. Soc.*, **38**, 1462, 1961.

Some theorems concerning generalised Hankel and Laplace transforms

By

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Abstract

A relation between a generalised Hankel transform of a function and a generalised Laplace transform of the product of this function with another function has been established. The Hankel transform considered is that given by Roop Narain and the Laplace transform that by Varma.

A theorem giving a relation between the Hankel transform of $f(x)$ and Meijer's Bessel function transform of $f(x) \cdot g(x)$ was given by Sharma⁴. The object of this note is to establish a relation between a generalised Hankel transform of $f(x)$ and a generalised Laplace transform of $f(x) \cdot g(x)$. The generalised Hankel transform considered here is the one given by Narain³ and the generalised Laplace transform that by Varma⁵.

The following notations will be used throughout this paper :

$$L\{f(x); p\} = \int_0^\infty e^{-px} f(x) dx \quad (1)$$

$$W_{k,m}\{f(x); p\} = \int_0^\infty (px)^{m-\frac{1}{2}} e^{-\frac{1}{2}px} W_{k,m}(px) f(x) dx \quad (2)$$

$$H_\nu\{f(x); y\} = \int_0^\infty (xy)^{\frac{1}{2}} J_\nu(xy) f(x) dx \quad (3)$$

$$H_\nu^{\lambda,\mu}\{f(x); y\} = 2^{-\nu} \int_0^\infty (xy)^{\nu+\frac{1}{2}} \chi_{\nu,\lambda,\mu}(xy) f(x) dx \quad (4)$$

$$\chi_{\nu,\lambda,\mu}(x) = x^{-\nu} G \frac{2,1}{2,4} \left(x \left| \begin{array}{l} \lambda - \mu - \frac{1}{2}, \nu - \lambda - \mu + \frac{1}{2} \\ \nu, \nu + 2\mu, 0 \end{array} \right. \right) \quad (5)$$

(2) reduces to (1) when $k + m = \frac{1}{2}$, because of the identity

$$z^{m-\frac{1}{2}} W_{\frac{1}{2}-m,m}(z) = e^{-\frac{1}{2}z}$$

(4) is a generalization of the Hankel transform denoted by

(3) and reduces to it when $\lambda + \mu = \frac{1}{2}$.

It has been established by Narain³ that

$$\chi_{\nu,\lambda,\mu}(x) \sim O(x^{\mu-\frac{1}{2}}) \text{ for small } x \quad (6)$$

and

$$\chi_{\nu, \lambda, \mu}(x) \sim O(x^{-\eta}) \quad \text{for large } x$$

where η stands for either of the three quantities

$$\frac{1}{2}(\nu + \frac{1}{2}), (\frac{1}{2} + \lambda - \mu), (\frac{3}{2} + \nu + \mu - \lambda).$$

Theorem 1

$$\text{If } Y^{\nu + \frac{1}{2} - \eta} \cdot H_{\nu}^{\lambda, \mu} \{ f(x); y \} \in L(0, \infty),$$

$$g(x) \in L(0, \infty),$$

$$R(\eta + \mu \pm \mu) > 0, R(\frac{1}{2} + \nu + m \pm m + \mu \pm \mu) > 0$$

$$\text{and } f(x) \cdot g(x) \cdot x^{m-\frac{1}{2}} \in L(0, R),$$

then

$$W_{k, m} \{ f(x) g(x); p \} = \int_0^\infty H_{\nu}^{\lambda, \mu} \{ f(x); y \} \cdot H_{\nu}^{\lambda-\mu} \{ (px)^{m-\frac{1}{2}} e^{-\frac{1}{2} px} W_{k, m}(px) g(x); y \} dy$$

Proof: Since [2, pp. 5]

$$f(x) = 2^{-\nu} \int_0^\infty (xy)^{\nu+\frac{1}{2}} \chi_{\nu, \lambda, \mu}(xy) H_{\nu}^{\lambda, \mu} \{ f(x); y \} dy$$

We have

$$\begin{aligned} & W_{k, m} \{ f(x) g(x); p \} \\ &= \int_0^\infty (px)^{m-\frac{1}{2}} e^{-\frac{1}{2} px} W_{k, m}(px) \cdot g(x) \left[\int_0^\infty 2^{-\nu} (xy)^{\nu+\frac{1}{2}} \chi_{\nu, \lambda, \mu}(xy) H_{\nu}^{\lambda, \mu} \{ f(x); y \} dy \right] dx \\ &= \int_0^\infty H_{\nu}^{\lambda, \mu} \{ f(x); y \} \cdot [2^{-\nu} \int_0^\infty (xy)^{\nu+\frac{1}{2}} \chi_{\nu, \lambda, \mu}(xy) \cdot (px)^{m-\frac{1}{2}} e^{-\frac{1}{2} px} W_{k, m}(px) g(x) dx] dy \\ &= \int_0^\infty H_{\nu}^{\lambda, \mu} \{ f(x); y \} \cdot H_{\nu}^{\lambda, \mu} \{ (px)^{m-\frac{1}{2}}, e^{-\frac{1}{2} px} \cdot W_{k, m}(px) g(x); y \} dy \end{aligned}$$

All that remains now is to justify the inversion of the order of integration. For this the integrals

$$\int_0^\infty \left| y^{\nu+\frac{1}{2}} \chi_{\nu, \lambda, \mu}(xy) H_{\nu}^{\lambda, \mu} \{ f(x); y \} \right| dy$$

and

$$\int_0^\infty |x^{\nu+m} e^{-\frac{1}{2} px} \cdot W_{k, m}(px) \chi_{\nu, \lambda, \mu}(xy) g(x)| dx$$

should be convergent and one of the repeated integrals must exist.

By virtue of (6) and (7), we have

$$y^{\nu+\frac{1}{2}} \chi_{\nu, \lambda, \mu}(xy) H_{\nu}^{\lambda, \mu} \{ f(x); y \} \sim y^{\nu+\frac{1}{2}-\eta} \cdot H_{\nu}^{\lambda, \mu} \{ f(x); y \} \quad \text{for large } y$$

and

$$\sim y^{\nu+\frac{1}{2}-\mu+\mu} H_{\nu}^{\lambda, \mu} \{ f(x); y \} \quad \text{for small } y.$$

Thus the y -integral is absolutely convergent when

$$y^{\nu+\frac{1}{2}-\eta} \cdot H_{\nu}^{\lambda,\mu} \{ f(x) ; y \} \in L(0, \infty)$$

and

$$R(\eta + \mu \pm \mu) > 0.$$

Again,

$$\begin{aligned} & x^{\nu+m} \cdot e^{-\frac{1}{2}px} W_{k,m}(px) \chi_{\nu,\lambda,\mu}(xy) g(x) \\ & \sim x^{\nu+m+k-\eta} e^{-px} g(x) \text{ for large } x. \\ & \sim x^{\nu+m \pm m + \mu \pm \mu + \frac{1}{2}} e^{-px} g(x) \text{ for small } x. \end{aligned}$$

The x -integral converges absolutely at the upper limit. Also, at the lower limit the integral converges absolutely if $R(\frac{1}{2} + \nu + m \pm m + \mu \pm \mu) > 0$.

Also the repeated integral exists if $f(x) \cdot g(x) \cdot x^{m-\frac{1}{2}} \in L(0, R)$. Therefore the inversion of the order of integration is justified under the conditions stated with the theorem by virtue of De La Vallee Poussin's theorem [1, pp. 504].

If we take $k + m = \frac{1}{2}$ in the theorem,

we obtain

Theorem 1(a)

If $y^{\nu+\frac{1}{2}-\eta} H_{\nu}^{\lambda,\mu} \{ f(x) ; y \} \in L(0, \infty)$

$g(x) \in L(0, \infty)$, $R(\eta + \mu \pm \mu) > 0$

$R(\nu + \mu \pm \mu + \frac{1}{2}) > 0$ and $f(x) g(x) \in L(0, R)$

Then

$$L\{f(x) g(x) ; p\} = \int_0^\infty H_{\nu}^{\lambda,\mu} \{ f(x) ; y \} \cdot H_{\nu}^{\lambda,\mu} \{ e^{-px} g(x) ; y \} dy$$

If we take $\lambda + \mu = \frac{1}{2}$ in the theorem,

we obtain

Theorem 1(b)

If $f(x)$ and $H_{\nu} \{ f(x) ; y \} \in L(0, \infty)$

$g(x) \in L(0, \infty)$, $R(m \pm m) > 0$

then

$$\begin{aligned} & W_{k,m} \{ f(x) g(x) ; p \} \\ & = \int_0^\infty H_{\nu} \{ f(x) ; y \} \cdot H_{\nu} \{ (px)^{m-\frac{1}{2}} e^{-\frac{1}{2}px} W_{k,m}(px) g(x) ; y \} dy \end{aligned}$$

If we further put $\lambda + \mu = \frac{1}{2}$ together with $k + m = \frac{1}{2}$ in the theorem, we obtain

Theorem 1(c)

If $f(x)$ and $H_{\nu} \{ f(x) ; y \} \in L(0, \infty)$, $g(x) \in L(0, \infty)$

and if $R(\frac{1}{2} + \nu) > 0$, $R(p) > 0$, then

$$L\{f(x) g(x) ; p\} = \int_0^\infty H_{\nu} \{ f(x) ; y \} \cdot H_{\nu} \{ e^{-px} g(x) ; y \} dy$$

We now illustrate the application of the last theorem by an *example*.

If we take $f(x) = x^{\mu-3/2} \sin(\alpha x)$ $[R(\mu) > -1]$

$$g(x) = x^{\frac{1}{2}},$$

then we have

$$L\{x^{\mu-1} \cdot \sin(\alpha x); p\} = \int_0^\infty H_\nu \{x^{\mu-3/2} \sin(\alpha x); y\} \cdot H_\nu \{e^{-px} \cdot x^{\frac{1}{2}}; y\} dy$$

or $\Gamma(\mu) \cdot (p^2 + \alpha^2)^{-\mu/2} \sin \left[\mu \tan^{-1} \left(\frac{\alpha}{p} \right) \right]$

$$= \int_0^\alpha \frac{y^{\nu+\frac{1}{2}} \cdot \Gamma(\nu+\mu) \sin \left\{ \left(\frac{\nu+\mu}{2} \right) \pi \right\}}{2^\nu \cdot \alpha^{\nu+\mu} \cdot \Gamma(\nu+1)} \cdot {}_2F_1 \left(\frac{1+\nu+\mu}{2}, \frac{\nu+\mu}{2}; \nu+1; \frac{y^2}{\alpha^2} \right)$$

$$\times (-1) y^{\frac{1}{2}-\nu} \cdot \frac{d}{dp} \left\{ \frac{[(p^2+y^2)^{\frac{1}{2}} - p]^{\nu}}{(p^2+y^2)^{\frac{1}{2}}} \right\} dy$$

$$+ \int_a^\infty \frac{2^\mu \cdot \alpha \Gamma(\frac{1}{2} + \frac{\nu}{2} + \frac{\mu}{2})}{y^{\mu+\frac{1}{2}} \Gamma(\frac{1}{2} + \frac{1}{2}\nu - \frac{\mu}{2})} \cdot {}_2F_1 \left(\frac{1+\nu+\mu}{2}, \frac{1+\mu-\nu}{2}; \frac{3}{2}; \frac{\alpha^2}{y^2} \right) \cdot (-1) y^{\frac{1}{2}-\nu} \frac{d}{dp} \left\{ \frac{[(p^2+y^2)^{\frac{1}{2}} - p]^{\nu}}{(p^2+y^2)^{\frac{1}{2}}} \right\} dy$$

when $R(p) > |\operatorname{Im} \alpha|$

or $\Gamma(\mu) (p^2 + \alpha^2)^{-\mu/2} \sin [\mu \tan^{-1} (\alpha/p)]$

$$= - \frac{\Gamma(\nu+\mu) \sin \left[\left(\frac{\nu+\mu}{2} \right) \pi \right]}{2^\nu \cdot \alpha^{\nu+\mu} \cdot \Gamma(\nu+1)} \int_0^\alpha y \frac{d}{dp} \left\{ \frac{[(p^2+y^2)^{\frac{1}{2}} - p]^{\nu}}{(p^2+y^2)^{\frac{1}{2}}} \right\} {}_2F_1 \left(\frac{1+\nu+\mu}{2}, \frac{\nu+\mu}{2}; \frac{\nu+\mu}{2}; \frac{y^2}{\alpha^2} \right) dy$$

$$- \frac{2^\mu \alpha \Gamma \left(\frac{1+\nu+\mu}{2} \right)}{\Gamma \left(\frac{1+\nu-\mu}{2} \right)} \int_a^\infty \frac{1}{y^{\nu+\mu}} \frac{d}{dp} \left\{ \frac{[(p^2+y^2)^{\frac{1}{2}} - p]^{\nu}}{(p^2+y^2)^{\frac{1}{2}}} \right\} {}_2F_1 \left(\frac{1+\nu+\mu}{2}, \frac{1+\mu-\nu}{2}; \frac{3}{2}; \frac{\alpha^2}{y^2} \right) dy$$

Similar examples can be constructed to illustrate the application of the other theorems.

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References

1. Bromwich, T. J. An introduction to the theory of infinite series. *Macmillan*, 1955.
2. Erdelyi, A. Tables of integral transforms, Vol. II : *Mcgraw Hill Co.*
3. Roop Narain. "On a generalization of Hankel transform and Self-reciprocal function". *Rend. Sem. Mat. Univ. Politec. Torino*, **16** : 269-300, 1957.
4. Sharma, K. C. "Theorems relating Hankel and Meijer's Bessel Transforms." *Proc. Glasgow Math. Assoc.*, **6** : 107-112, 1963.
5. Varma, R. S. "On a generalisation of Laplace Integral". *Proc. Nat. Acad. Sc., (India)*, **A20** : 209-216, 1951.

Talc as a medium of growth for Nitrate-forming Bacteria

By

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Abstract

The effectiveness of talc alone, as well as in presence of carbonates of Ca, Ba, Sr, Mg, and Na as a medium of growth for Nitrobacter has been studied, and it has been found that talc when used alone or when used along with carbonates of Ba and Sr, is not a suitable medium for the growth of Nitrobacter, but when it is used along with optimum amounts of carbonates of Ca, Mg and Na, it acts as a fairly satisfactory medium. Among the carbonates, Na_2CO_3 has been found to be the best, while BaCO_3 is the worst, probably being toxic.

Introduction

In 1890 Winogradsky¹ observed that nitrifying bacteria could not be isolated on agar, gelatin and peptone media, although these media had been found very useful for the isolation of other bacteria in general. This led to the belief that in presence of organic matter nitrifying bacteria are probably not active and hence their isolation on organic matter is not possible. However, Winogradsky succeeded in isolating a pure culture of these bacteria by plating on a completely inorganic medium solidified with silica gel. Since then many inorganic media² with various modifications have been suggested for the isolation and cultivation of nitrifying bacteria.

Tandon, De and Rastogi^{3,4,5} and Khare⁶ employed various clay minerals namely bentonite, vermiculite, pyrophyllite and talc as media of growth for Nitrosomonas and found that these can be used as media of growth for Nitrosomonas, if these clay minerals are used along with carbonates of magnesium, calcium, strontium and barium in the proper ratio. They further showed that MgCO_3 serves better as compared to carbonates of Ca, Sr and Ba.

In order to see, if these clay minerals can be used as a medium of growth for Nitrobacter also, we have carried out detailed experiments. The results with talc when used alone and when used along with carbonates of Mg, Ca, Sr, Ba and Na are discussed here.

Experimental

A pure culture of nitrate-forming bacteria was isolated from the soil by the usual elective culture method employing Fred and Davenport's medium.

The following solutions were taken :

Solution A—Sterilized sodium nitrite solution containing one milligram nitrogen per ml.

Solution B—Containing all the constituents of Fred and Davenport's medium except sodium nitrite.

For the systematic study, four sets, each comprising of four 250 ml Jena flasks were taken. In each flask of every set 1·0, 1·5, 2·0 and 2·5 gm talc was taken separately. Into each of the three flasks of every set 0·01, 0·05 and 0·10 gm $MgCO_3$ was introduced separately. The fourth flask of each set was left as such with no carbonate. 50 ml distilled water was then added to the contents of each flask. One more flask with 50 ml. solution B was also taken. 0·2 ml. sodium nitrite solution was then added to each of the above flasks. All the flasks were sterilized at 15 lb pressure for 15 minutes in an autoclave. After sterilization the flasks were allowed to cool and then a definite amount of the inoculum was introduced into each of the flasks which were then kept in an incubator.

Nitrite was estimated in each flask after every 48, 96, 168, 240 and 360 hours by Griess-Ilosovay method.

Discussion

The amount of total nitrite and nitrate nitrogen was also estimated at the beginning and at the end of each experiment, and it was found that the total remained the same, which thereby clearly indicated that there was no loss of nitrogen during the process of nitrite oxidation and the nitrite which disappeared changed only to nitrate.

The results obtained indicate that when talc alone is used as a medium of growth for Nitrobactor the nitrite oxidation is less than when Fred and Davenport's medium is used. Maximum nitrate formation takes place when 2·0 gm talc is present per 50 ml. In the talc medium out of the 0·2 mg nitrogen taken in the beginning in the form of nitrite, 0·007986 mg was left even after 360 hours, whereas in Fred and Davenport's medium 0·004356 mg only was left after 168 hours.

It is further observed that the addition of carbonates of Mg, Ca, and Na to talc makes the latter a more effective medium and causes an increase in the rate of nitrate formation, but even this increased rate is lower than that which obtains in Fred and Davenport's medium. Among the carbonates used Na_2CO_3 was found to produce maximum increase in nitrate formation, and this was with a solution containing 2·0 gm talc and 0·05 gm Na_2CO_3 . In this solution nitrogen left after 168 hours was found to be 0·01742 mg, while with Fred and Davenport's medium under similar conditions and in the same time, the amount of nitrite nitrogen left was only 0·004356 mg.

The growth on talc in the presence of $MgCO_3$ and $CaCO_3$ is also fair; it is slightly better with $MgCO_3$, although the difference between the two is not much. After 168 hours of bacterial activity 0·04792 mg nitrite nitrogen was left in the medium containing 2·0 gm talc and 0·10 gm $MgCO_3$, while 0·052998 mg nitrite nitrogen was left in the medium containing 2·0 gm talc with 0·05 gm $CaCO_3$.

Our study further shows that talc along with carbonates of strontium and barium is not a good medium for the growth of nitrate-formers. This growth in the presence of both barium carbonate as well as strontium carbonate is very slow. For instance, in the presence of 2·0 gm talc and 0·01 gm. $SrCO_3$ after 240 hours of bacterial activity 0·04138 mg nitrite nitrogen was left, whereas in the case of Fred and Davenport's medium only 0·004356 mg nitrite nitrogen was left after only 168 hours of bacterial activity.

The presence of barium carbonate in the medium has been found to be injurious and the growth starts decreasing with the addition of even the smallest quantity of BaCO_3 .

Thus, it is clear that talc when used alone or when used along with carbonates of strontium and barium is not a good medium for the growth and activity of nitrate-forming bacteria, but talc along with carbonates of sodium, calcium and magnesium can be successfully employed for the cultivation and isolation of these bacteria. The effectiveness of talc with different carbonates may be put as follows :



References

1. Stanier, R. Y., Doudoroff, M. and Adelberg, E. A. "General Microbiology" Ed. 1958.
2. Fred, E. B. and Waksman, S. A. "Laboratory manual of general microbiology with special reference to the microorganisms of the soil." Ed. 1928.
3. Tandon, S. P., De, S. K. and Rastogi, R. C. "Nitrosification in vermiculite medium." *Vijnana Parishad, Allahabad, India*, 5 (2) 83-88, 1962.
4. Tandon, S. P., De, S. K. and Rastogi, R. C. "Bentonite as a Growth medium for Nitrite-forming bacteria (Nitrosomonas) : Part I." *N. Jb. Miner. Mh.* 2, 42-47, 1962.
5. Tandon, S. P., De, S. K. and Rastogi, R. C. "Bentonite as a Growth Medium for Nitrite-forming bacteria (Nitrosomonas) : Part II." *Proc. Nat. Acad. Sci. India*, A-34 (1), 15-21, 1964.
6. Khare, H. P., D.Phil. Thesis, Allahabad University, 1965.

Proanthocyanidins of *Symplocos racemosa* Bark Part I

By

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Two glycosides have been isolated from the ethanolic extract of *Symplocos racemosa* (stem bark). On the basis of chemical and spectral studies one of these has been assigned a structure as the 3-monoglucosuranoside of 7-O-methyl leucopelargonidin. The other water soluble glycoside is closely related to the above one.

*Symplocos racemosa*¹ commonly known in Hindi as 'Lodh tree' and in English 'Californian Cinchona' is widely distributed throughout the northern region of India. The most important part of the plant is the rough acrid stem-bark which is astringent in taste and is reported for its great medicinal importance. It has been reported to be useful in eye diseases, blood diseases, cough, dysentery, inflammation, bowel complaints, spongy gums and ulcers. Despite the great medicinal value very little work has been done so far to study its constituents. The presence of three alkaloids in the bark was reported by Hesse², which were named as Loturine 0·24%, Loturidine 0·06% and Colloturine 0·02%. Later on Spath³ showed that these compounds were identical to abrine and harmala.

In order to carry out a systematic investigation, the powdered stem-bark, already extracted with benzene, was put for extraction with boiling ethanol. From the concentrated extract two compounds were isolated. One (Compound A) was sparingly soluble in water and the other (Compound B) could be extracted out with ethyl acetate from the aqueous solution. Both these compounds were repeatedly crystallised and their homogeneity was confirmed on paper and thin layer chromatography. The compound (A) on heating with ethanolic hydrochloric acid gave a deep red solution. This colour could be extracted out with amyl alcohol and on addition of sodium acetate turned purple, and again changed to red on addition of hydrochloric acid. It behaves exactly like natural anthocyanidins. Hence the conclusion could be drawn that the original compound may be a leucocyanidin. Further, the compound gave positive Molisch test, indicating the presence of a sugar moiety in the molecule. It did not respond to positive test with aniline hydrogen phthalate⁴, which is a specific reagent for free aldehyde group. This suggested that the reducing group of the sugar is involved in linking and is not free. With ferric chloride the compound gave dull brown colour, which eliminated the possibility of the presence of any free catechol or pyrogallol unit in the molecule.

The compound (A) on acid hydrolysis gave an anthocyanidin and a sugar. The sugar was identified as glucose by paper chromatography, TLC and by preparing its phenylosazone and finally comparing with authentic glucose. The anthocyanidin obtained gave colour tests similar to simple anthocyanidins, but did not show any characteristic colour with ferric chloride. Its *Rf*-value on paper was higher than that of pelargonidin in Forrestal solvent. This indicated that it must have lesser number of free hydroxyls than pelargonidin.

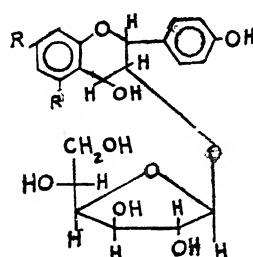
The λ_{max} in ethanolic hydrochloric acid was at $530m\mu$ (pelargonidin has λ_{max} at $535m\mu$). In case of anthocyanins it is generally known that substitution of one hydroxyl group lowers the λ_{max} by $5m\mu$ to $10m\mu$. Hence, the conclusion could be drawn that may be one of the hydroxyls in pelargonidin is substituted by some group. With aluminium chloride, there was no bathochromic shift confirming thereby the absence of any catechol unit in the molecule.

The I. R. of the glycoside and its acetate both show peak for methoxyl group ($\delta_{max} 1280 \text{ cm}^{-1}$). The NMR also confirmed the presence of methoxyl group. Methoxyl estimation shows the presence of only one methoxyl group.

In order to find out the position of $-OCH_3$ group in the molecule, the glycoside was subjected to neutral permanganate oxidation when p-hydroxy benzoic acid was isolated as a product. This observation excluded the possibility of the presence of methoxyl group in the side phenyl. There was one choice left i.e. methoxyl may be either at 5 or 7 positions of the pelargonidin nucleus. On the basis of biogenesis it is more likely to be in 7-position, 5-position being free, as indicated by a shoulder at $450m\mu$ in the visible spectrum of the corresponding anthocyanidin. Hence, the sugar may be either at 3 or 4 positions (diol unit).

Another point to be decided was, whether sugar moiety is present here as a monosaccharide or a disaccharide or polysaccharide chain. It was decided by subjecting the glycoside methyl ether to periodate oxidation. One mole of the compound consumed two moles of periodate, without the formation of formic acid, an observation which can only be explained if there is only one glucose unit present, and that too in the furanose form. If it was in the pyranose form, formic acid would have been obtained.

Enzymatic hydrolysis of the glycoside with emulsin suggested the nature of the linkage as β . However, the position of the glycoside linkage was determined by subjecting the glycoside to catalytic hydrogenation, when no free sugar was obtained. This excluded the possibility of its being present as benzylic hydroxyl in the 4-position. On the basis of biogenesis and parallelism with anthocyanins, the position for sugar was decided to be at 3. Hence, the glycoside has been assigned the structure I (a), although the alternative structure I (b) cannot be totally excluded.



I (a) $R = OCH_3$; $R' = OH$
 (b) $R = OH$; $R' = OCH_3$

There are two novel features in this glycoside. It is the first time that leucopelargonidin is reported to be present in nature in the form of its glycoside and secondly none of the proanthocyanidins so far reported have been found to be partial or full methyl ethers. In leucoanthocyanidins, this is the first case of a partial methyl ether being reported to be present in nature. This glycoside which is highly astringent in taste, might explain, the medicinal properties possessed by the bark.

Experimental

*Extraction of the stem bark of *symplocos racemosa* :*

The benzene extracted powdered stem bark of *symplocos racemosa* (1 kg.) was extracted with hot 95% ethanol thrice. The combined extract was concentrated under reduced pressure when almost all the alcohol distilled off. The concentrate was poured over excess of water with constant stirring, when a brown amorphous mass (I) separated, it was washed several times with cold water. The washings and filtrate (II) were mixed and extracted with ethyl acetate continuously.

The amorphous mass (I) so obtained was macerated with cold acetone, the insoluble sticky matter was removed and from the acetone soluble fraction a buff coloured semi-crystalline compound was obtained on repeated crystallisation from acetone-ethyl acetate mixture. The compound did not melt but decomposed at 240°C and its purity was tested on thin layer chromatography using silica gel plate (solvent : butanol : 2N/HCl, 1 : 1). The compound was sparingly soluble in ether and light petrol and readily dissolved in ethanol, methanol, acetone and dioxan, Rf 0.73 (butanol : 2N HCl 1 : 1); λ_{max} 275m μ .

Acid hydrolysis

The glycoside (.02 g) was refluxed with 5% ethanolic hydrochloric acid (10 ml) for 2 hrs. The deep red solution obtained was diluted with water (20 ml) and phlobaphene which separated out was filtered off and the filtrate was extracted thrice with small amounts of amyl alcohol. The anthocyanidin was transferred to 1% aqueous hydrochloric acid solution by shaking the amyl alcoholic solution with excess of light petroleum. The acid layer was washed with petrol and then with benzene to get rid of all the traces of amyl alcohol. To it excess of conc. hydrochloric acid was added, when a deep maroon coloured solid was obtained which gave tests for anthocyanidins. It gave purple colour with sodium bicarbonate and carbonate which turned red on addition of acid, and dull brown colour with ferric chloride. It gave single spot on paper Rf = .78 (solvent - Forrestal), (pelargonidin, Rf 0.63). λ_{max} in 0.1% ethanolic hydrochloric acid 530m μ (Pelargonidin λ_{max} , 535m μ). There was no shifting of maxima on addition of aluminium chloride indicating thereby the absence of o-dihydroxy grouping in the molecule.

Sugar :

The acidic solution after extraction with amyl alcohol was neutralised with barium carbonate and concentrated on a water bath. The concentrated syrup gave positive Molisch test, reduced Fehling's solution and on paper showed a single spot Rf = .19 (solvent ; butanol/acetic acid/water (4 : 1 : 5); spray : A. H. P.). Authentic sample of glucose under identical conditions gave Rf = .18. This was further confirmed to be glucose by comparing with an authentic sample on a TLC plate of silica gel in boric acid (0.1N), (solvent ; n-propanol/ammonium hydroxide/water (6 : 2 : 1), spray ; A. H. P.)

Osazone :

To the concentrated sugar solution excess of phenylhydrazine hydrochloride, sodium acetate solution and saturated sodium bisulphite solution were added. On heating the mixture for 5 minutes on a water bath osazone appeared as deep yellow needles m.p. 202 - 4°. The authentic phenylosazone of glucose had same crystalline form and m.p. 205°C.

Acetylation :

The glucoside (0.02 g) was dissolved in a mixture of acetic anhydride (5 ml) and pyridine (0.5 ml) and kept at room temperature for 48 hours, then poured over crushed ice and left overnight. The colourless solid obtained was filtered, washed with water and crystallised from ethyl acetate-light petroleum mixture as light yellow crystals (m.p. 210–212° decomp.).

Methylation :

The glycoside (0.025 g) was suspended in dry acetone (30 ml), freshly ignited potassium carbonate (1 g) and dimethyl sulphate (1 ml) was added and the solution was refluxed for 6 hrs. It was cooled, potassium salt was filtered and washed with acetone. The combined filtrate and washings were concentrated and poured over crushed ice and left overnight. The colourless solid obtained was filtered, washed with water and crystallised from ethyl acetate-light petroleum mixture as pale yellow semi-crystalline solid m.p. 225° (decomp.).

Acetylation of methylated glycoside :

The methyl ether of the glucoside (30 mg) was treated with acetic anhydride (5 ml) and freshly ignited sodium acetate (20 mg) was added and the mixture was heated at 130 – 140°C for 1.5 hours. It was cooled, filtered and poured over crushed ice and kept overnight. The light yellow solid obtained was filtered, taken in ethyl acetate from which the coloured impurities were removed by fractional precipitation with light petroleum and finally the acetate was obtained as a pale yellow crystalline solid. It crystallised from ethyl acetate – light petroleum mixture as light yellow crystals m.p. 112 – 15°C (decomp.).

Potassium permanganate oxidation :

A boiling solution of the glycoside (50 mg) in acetone (50 ml) was treated during 5 hours with powdered potassium permanganate (2.5 gm) in small lots. It was cooled, water added and most of the acetone was removed by distillation and sulphur-di-oxide gas passed to dissolve all manganese-di-oxide and excess permanganate. The clear slolution was extracted with ether and the extract was washed with aqueous saturated sodium bicarbonate. The bicarbonate solution was acidified with hydrochloric acid and then repeatedly extracted with ether. On concentration the ether extract gave *p*-hydroxy benzoic acid as shown by paper chromatography, R_f, 0.23 (solvent : butanol saturated with ammonia). R_f. for authentic sample of *p*-hydroxy benzoic acid under identical conditions is 0.26. This was further confirmed by TLC on silica gel G. plate (solvent, ethanol/water/ammonium hydroxide (100 : 12 : 15).

Periodate Oxidation (Quantitative)

The methyl ether of the glycoside (0.01051 g) was dissolved in aldehyde free ethanol (20 ml) and to it sodium metaperiodate solution (10 ml, 2.4372 g/250 ml) was added. A blank was similarly run. Both were kept at room temperature for 48 hours. To 5 ml of this reaction mixture, excess of standard sodium arsenite solution (10 ml, 2.6627 gms. arsenious oxide per 250 ml) was added and the mixture was kept at room temperature for 15–20 minutes. It was titrated against standardised iodine solution (10 ml of sodium arsenite ≡ 16.88 ml of iodine solution); when the volume consumed was 12.28 ml. In the blank titration the volume of iodine consumed was 12.04 ml. From these readings, the amount of sodium metaperiodate consumed was calculated to be 2.2 moles for one mole of the glycoside methyl ether.

5 ml of the reaction mixture was separately titrated against 0·01 N sodium hydroxide solution (standardised against oxalic acid solution) using methyl red as an indicator, but there was no consumption of alkali. This showed that formic acid was not produced in the reaction.

Enzymatic hydrolysis with emulsin :

The glycoside (0·02 g) was dissolved in aqueous ethanol (20 ml; 3 : 1) and to this emulsin solution (25 ml), prepared from almonds⁵, was added and the mixture kept in a water bath, maintained at 45°C, for 4 days. Then the mixture was extracted with ethyl acetate twice. The ethyl acetate extract was washed with water. On paper chromatography, it gave a single spot, $R_f = 0\cdot70$ (solvent, *n*-butanol : acetic acid : water (4 : 1 : 5), lower phase ; spray, vanillin hydrochloric acid reagent). This fraction was free from sugar as indicated by negative Molisch test. The aqueous solution, left after extraction with ethyl acetate, was concentrated on a rotary evaporator and the syrup on paper chromatography, gave a single spot $R_f = 0\cdot18$ (solvent, *n*-butanol : acetic acid : water (4 : 1 : 5), upper phase : spray, aniline hydrogen phthalate). Glucose under similar conditions gave the same $R_f = 0\cdot18$. Mixed paper chromatography gave a single spot.

Hydrogenation :

The glycoside (0·02 g) was dissolved in ethanol (40 ml) and platinum oxide (0·05) was added. The hydrogenation was carried out at atmospheric pressure for 4 hours. The resulting solution did not reduce Fehling's solution and did not show the presence of any free sugar. On filtering off the catalyst and evaporating the solvent, the glycoside could be recovered back unchanged, as shown by the m.p. and paper chromatography.

Next, it was put for hydrogenation under 15 lbs pressure for 5 hours, but even then, there was no hydrogenation and glycoside could be recovered back unchanged.

Isolation of glycoside (B) from the aqueous extract

The aqueous extract (II) was continuously extracted with ethyl acetate and the yellow extract concentrated under diminished pressure and light petroleum added slowly to separate sticky impurities first and later a buff coloured semi crystalline glycoside was obtained. It gave colour reactions similar to the above glycoside (A).

Acknowledgement

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References

1. Basu, B. D. and Kirtikar, K. R. Indian Medicinal Plants Vol. II, 1936, p. 1510; Chopra, Nayar and Chopra. *Glossary of Indian Medicinal Plants*, p. 237, 1956.
2. Hesse, O. *Deut. Chem. Ges. Ber.* II, 1542–46, 1878.
3. Spath, Monatsch, 41, 401–3, 1920.
4. Hough, L., Jones, J. K. N. and Wadman, W. H. *J. Chem. Soc.*, 1702, 1950.
5. Mann, Frederick G., Saunders, Bernard Charles. *Pract. Org. Chemistry*, p. 513.

An Spectroscopic investigation of complex formation in Cobalt (II) Chloride-aliphatic amine system

By

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Abstract

Visible absorption spectra of cobalt (II) chloride and various aliphatic amine solutions were analysed, with a view to extract information regarding each of amine-cobalt (II) complex. Presence of 6 different complexes i.e. mono, di, tri, tetra, penta and hexamines have been indicated by the shift in the position of absorption maxima. The energy changes of these complexes due to exchange of water ligands with amines, have been calculated and an interpretation is offered for this shift in the position of absorption maxima.

Introduction

A survey of the literature shows that ammonia complexes of cobalt (II) chloride have been investigated. However, aliphatic amines have been given very little attention^{1,2}. In the present paper the result obtained by a systematic spectroscopic investigation of cobalt (II) chloride solutions with different molar quantities of amines are reported. Amines used are methyl, ethyl, propyl, butyl, dimethyl, diethyl and dipropyl amines.

Experimental

The spectra were obtained with a Unicam Sp500 spectrophotometer on 2×10^{-2} cobalt chloride solutions with different molar quantities of aliphatic amines. The pH of the solution was buffered at low value with approximately 2M ammonium chloride solution.

Results

The value of absorption maxima, energy observed per mole and intensity of various complexes formed by different aliphatic amines have been given in table 1.

Discussion

It is reported that complex formation in solution is a stepwise process and many of the complexes so formed are quite stable, so that they can be studied upto certain extent³. It has therefore been found that gradual addition of ammonia

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TABLE I

Amine used	Monoamine			Diamine			Triamine			Tetramine			Pentamine			Hexamine		
	V ₂ in Molar 10 ⁻⁵ m μ	E ₁ × absorb	V ₂ in Molar 10 ⁻⁵ m μ	E ₂ × absorb	V ₂ in Molar 10 ⁻⁵ m μ	E ₃ × absorb	V ₂ in Molar 10 ⁻⁵ m μ	E ₄ × absorb	V ₂ in Molar 10 ⁻⁵ m μ	E ₅ × absorb	V ₂ in Molar 10 ⁻⁵ m μ	E ₆ × absorb	V ₂ in Molar 10 ⁻⁵ m μ	E ₇ × absorb	V ₂ in Molar 10 ⁻⁵ m μ			
1. Ammonia	550	10·1	2·137	540	10·12	2·216	525	10·20	2·280	505	10·40	2·370	485	10·70	2·468	460	11·20	2·602
2. Methyl- amine	552	10·15	2·169	540	10·15	2·216	528	10·25	2·267	506	10·45	2·366	486	10·75	2·460	461	11·22	2·599
3. Ethyl- amine	550	10·08	2·161	542	10·156	2·210	526	10·26	2·275	505	10·45	2·370	485	10·75	2·468	465	11·25	2·574
4. Propyl- amine	555	10·085	2·151	542	10·154	2·210	525	10·28	2·280	506	10·40	2·366	488	10·70	2·453	450	11·20	2·658
5. Butyl- amine	558	10·089	2·146	539	10·160	2·220	525	10·27	2·280	504	10·48	2·375	485	10·78	2·468	450	11·20	2·658
6. Dimethyl- amine	560	10·100	2·140	540	10·165	2·216	527	10·20	2·270	505	10·49	2·370	489	10·79	2·442	455	11·25	2·630
7. Diethyl- amine	558	10·100	2·146	542	10·100	2·210	526	10·220	2·275	505	10·48	2·370	488	10·78	2·453	460	11·25	2·602
8. Dipropyl- amine	558	10·120	2·146	540	10·089	2·216	525	10·200	2·280	506	10·40	2·366	485	10·80	2·468	458	11·30	2·591

or amines to a copper or nickel sulphate solutions, results in the formation of 4 and 6 different complexes respectively, each of which shows a definite absorption maximum and these are named as mono, di, tri, tetra, penta and hexamines depending upon the number of amine molecules that they contain^{4,5}.

If ammonia or other aliphatic amines are added to the cobalt solution, it has been observed that the colour of the solution changes from pink to pink blue indicating the gradual formation of hexamine. For the spectrophotometric study of the solutions, exactly one mole of various amines are added to cobalt (II) chloride solution in water. Since at each integral ratio a number of species exist in appreciable quantity, the value of the actual absorption maximum in each case, was found as in case of copper and nickel complexes^{4,5} by plotting true absorptivity against wavelength, latter being obtained by solving the equation

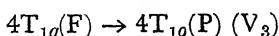
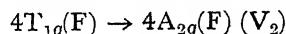
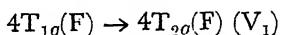
$$AS_i^\lambda = b \sum_k a_k^\lambda C_{ki}$$

Where AS_i^λ is the absorption at wavelength λ for the i^{th} $(\text{Amine})_o / (\text{Cobalt})_o$ ratio, b is the cell thickness a_k^λ is the absorptivity index for the K^{th} species at λ and C_{ki} is the concentration of the K^{th} compound at i^{th} ratio.

Each complex exhibits two absorption bands, one very sharp and another shoulder and their relative band shifts if compared to cobalt (II) chloride, by the addition of different molar quantities of amine solutions, indicate the gradual formation of mono, di, tri, tetra, penta and hexamine cobalt (II) chloride complexes. The addition of amine even in excess, later on causes no change in the position of the bands

The energy in K. cals absorbed per mole of each complex, for every absorption band, has been calculated by the formula $E = NhC/\lambda$, where N is Avogadro's Number, h is Planck's constant, C velocity of light and λ the wavelength of complex under consideration. It is observed that as the water ligands are replaced by various amines there is a gradual change in the various energy values. It is further noted that the energy values in different complexes are constant and are unaffected by the increasing molecular weight of the amine.

Cobalt (II) chloride exists in solution as $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$ ion and contains octahedrally co-ordinated cobalt (II). The Co^{+2} ion has the electron configuration d^7 and its ground state in an octahedral field is represented by $t_{2g}^6 e_g$ in strong fields (water or amines). Under the influence of a very strong octahedral field, a $2E$ state originating from the $2G$ state of the free ion will become the ground state. Such complexes possess only three spin allowed d-d transitions, which are represented as V_1 , V_2 and V_3 and assigned as follows :



The main band of the spectra is the V_2 band and the shoulder is V_3 . From the above assignments, V_1 is expected to lie in the near infra red and therefore escapes detection. The bands possess low molar absorbance values.

In case of hexaquo cobalt (II) ion the solution is pink in colour and the V_2 band is observed at $550 \text{ m}\mu$ while the V_3 band at $495 \text{ m}\mu$ as a slight shoulder. When amines are added the replacement of water ligands with amines, which lie toward the stronger end of spectrochemical series, begins and the colour of the

solution changes. The position of the V_2 absorption band shifts to lower wavelength or higher frequency region while the V_3 shoulder occupies the same position. With a subsequent increase in ligand field than water gives rise to an hypsochromic effect, which causes the absorption band to shift to lower wavelength. The energy now available for the electron to jump from one level to another is consequently increased, but this can not cause any apparent change in the magnitude of the transitions, because the above mentioned three transitions are the only spin-allowed transitions for bivalent cobalt in an octahedral field. It is thus concluded that the change in the position of absorption maximum is due to the stronger ligand field environment produced around the metal by the replacement of water with amines.

References

1. W. E. Hatfield and J. T. Yoke. *Inorg. Chem.*, **1**, 463, 1962.
2. S. Prasad, Y. M. Reddy and M. R. Seethapathy, *J. Ind. Chem. Soc.*, **42**(1), 46, 1965.
3. J. Bjerrum. Metal amine formation in aqueous solution (F. Hasse and Sons), 1941.
4. Padmaja Shukla. *J. Prakt. Chem.* in press.
5. Padmaja Shukla and Gopal Narain. *J. Prakt. Chem.*, **4**(38), 289, 1968.

Effect of Nitrogen and Phosphorus on the Composition of Oat

By

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Abstract

The effect of nitrogen and phosphorus on the composition of oat was studied under field conditions. The results indicate that the crude fibre percentage increased, whereas percentage of phosphorus, crude fat and mineral matter decreased with advancement in maturity of the crop. Phosphorus application @ 30 lbs./acre proved beneficial over control. Nitrogen application decreased the crude fibre content, but increased the crude fat, phosphorus and mineral matter contents of the plants. A combination of $P_{30}N_{60}$ and variety 'Green Mountain' proved to be the best treatment.

Studies in chemical composition of plants are of paramount importance judging from the quality of crop and the fertility status of soil. Such studies help in characterization of soil chemical properties in terms of plants.

The purpose of this study was to obtain information of average content of phosphorus, crude protein, crude fat and mineral matter, at seven stages of growth of oat, the total uptake of phosphorus and the total production of crude fibre, crude fat and mineral matter per acre, by grain and straw separately.

Experimental

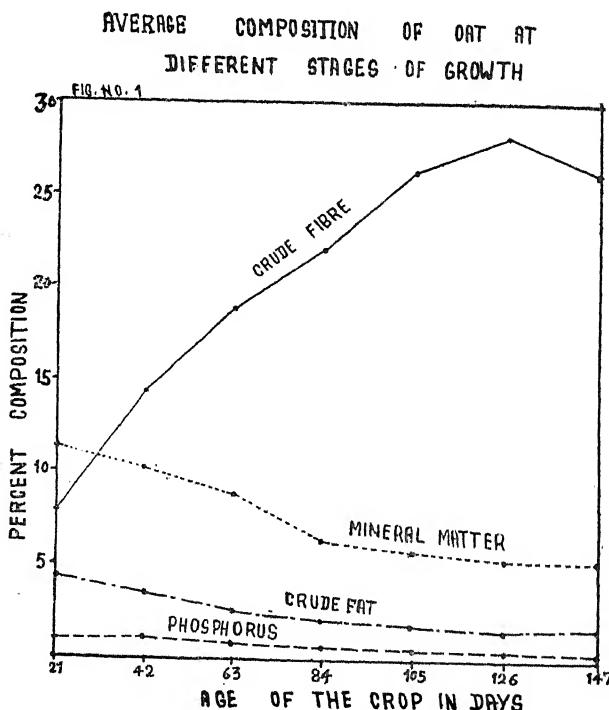
The experiment was conducted at the Students' Instructional Farm, Govt. Agricultural College, Kanpur, during Rabi season, 1964-65. Two varieties of oat, i.e. "Green Mountain" and "Oat-11" were sown at the rate of 30 kgs. per acre on 10th November, 1964. The design of the experiment was split-plot with 4 replications in which phosphorus was the main factor with two levels, i.e., 0 and 30 lbs. per acre. It was applied at the time of sowing the crop. Nitrogen with 4 levels, i.e., 0, 30, 60 and 90 lbs. per acre along with two varieties, were the sub-factors. The combination of nitrogen and varieties were applied in each subplot of the main plots with the help of random number, with a view to know the best variety and suitable dose of nitrogen. Half of the amounts of nitrogen were applied as basal dressing, and rest were topdressed with irrigation, 60 days after sowing.

The composite samples of four plots of the similar treatment-combinations from each block were taken at an interval of 21 days. The total number of samplings were 7, during the whole period of crop growth. In the last sampling the grain and straw were studied separately.

Phosphorus was determined by colorimetric method, i.e., "chlorostannous reduced molybdophosphoric blue colour method in hydrochloric acid system, as described by Jackson (1957). Crude fibre was determined by standard method as described by Piper (1950). Crude-fat was extracted with petroleum ether, using Soxhlet's apparatus as described by Piper (1950). The mineral matter was determined by dry ashing of the plant material.

TABLE I
Average percentage of phosphorus, crude-fibre, crude-fat and mineral matter at different stages of growth

Sl. No. of sampling	1	2	3	4	5	6	7	
Age of the crop in days	21	42	63	84	105	126	147	
Stage of growth	4 leaves stage	6-7 leaves stage	Boot stage	Heading stage	early milk stage	early dough stage	Harvesting stage	
Part analysed	whole plant	whole plant	whole plant	whole plant	whole plant	whole plant	Grain	Straw
1. Phosphorus	0.930	1.058	0.773	0.669	0.538	0.457	1.022	0.183
2. Crude fibre	7.74	14.42	18.94	22.07	26.25	28.07	10.93	32.24
3. Crude fat	4.31	3.55	2.58	2.09	1.75	1.55	4.44	1.43
4. Mineral matter	11.28	10.23	8.82	6.26	5.85	5.29	7.86	4.78
								whole plant



FIGNO.2

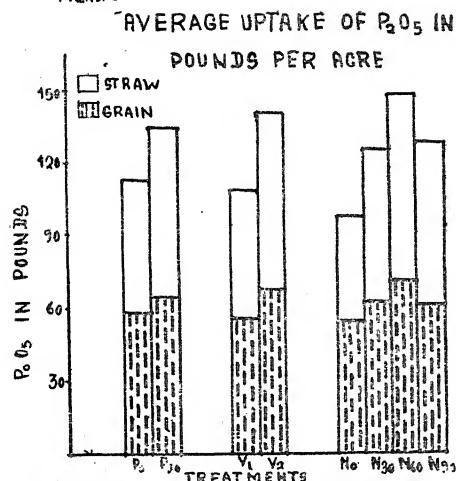


FIG NO.3 AVERAGE CRUDE FIBRE IN POUNDS PER ACRE

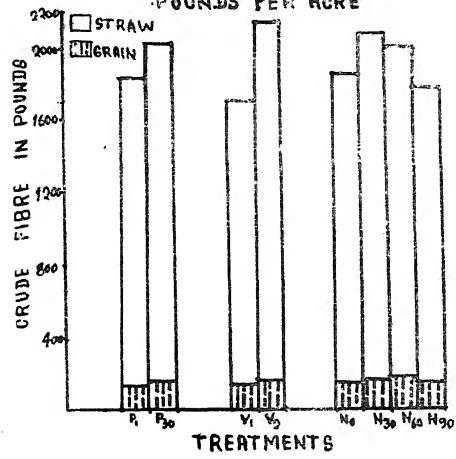


FIG.NO.4

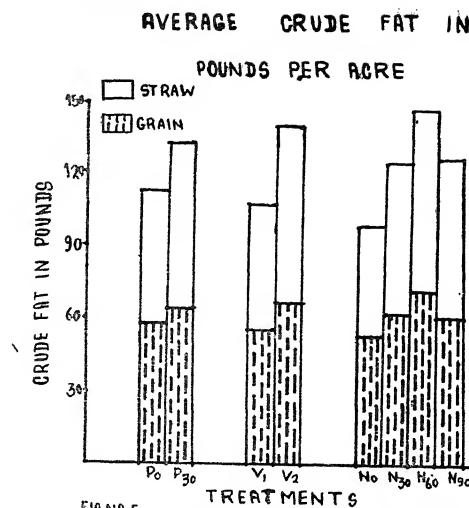
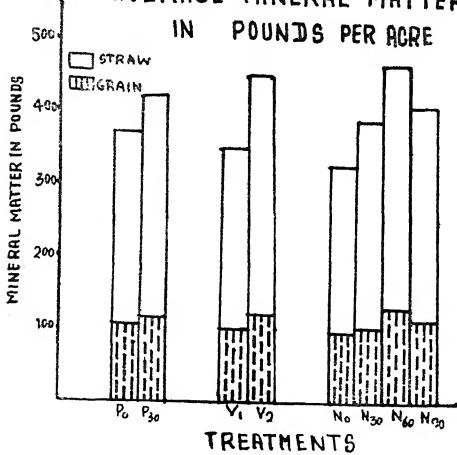


FIG NO.5 AVERAGE MINERAL MATTER IN POUNDS PER ACRE



Results and Discussion

A complete picture of 7 stages of growth and the average percentage of phosphorus crude fibre, crude-fat and mineral matter is given in Table No. 1 and Fig. No. 1.

It is evident from table No. 1 and Fig. No. 1 that phosphorus percentage of plants slightly increased in second sampling and then decreased upto the maturity. The percentage of P_2O_5 was found higher in grain than in straw. The percent crude fibre increased rapidly during the period of early-growth, until the early dough stage, due to the conversion of simple sugar into cellulose, hemicellulose and lignin. Thereafter, the percent crude fibre decreased slowly. The grain had lower percentage of crude fibre than straw. The crude fat and mineral matter percentages decreased slowly with the maturity of the crop. The grain had higher

percentage of crude fat and mineral matter than straw. These results are in conformity with the results obtained by Berry (1920), Smith (1960), Stola (1937) and Stall-cup (1960).

In general, differences in phosphorus, crude-fibre, crude-fat and mineral matter contents of plant, due to date of samplings, are significant. There is negative correlation between the crude fibre and crude fat percentage. But the crude fat, phosphorus and mineral matter are positively correlated.

TABLE 2
Average uptake of P₂O₅ in pounds per acre

Treatments	Uptake of P ₂ O ₅		Total	Intensity of increment
	Grain	Straw		
P ₂ O ₅ Levels	(P ₀)	13.05	7.27	20.32
	(P ₁)	14.85	14.70	29.56
Varieties	(V ₁)	12.81	9.52	22.33
	(V ₂)	14.87	12.42	27.29
Nitrogen levels	(N ₀)	12.90	8.95	21.85
	(N ₁)	14.05	11.06	25.11
	(N ₂)	15.35	12.76	28.11
	(N ₃)	13.52	11.17	24.69
Total Percentage		111.40	87.85	199.25
		55.90	44.10	100

TABLE 3
Average crude fibre in pounds per acre

Treatments	Crude fibre		Total	Intensity of increment
	Grain	Straw		
P ₂ O ₅ levels	(P ₀)	147.59	1682.21	1829.80
	(P ₁)	154.18	1866.21	2020.39
Varieties	(V ₁)	140.76	1564.61	1705.37
	(V ₂)	162.06	1981.66	2143.72
Nitrogen levels	(N ₀)	155.50	1692.80	1848.30
	(N ₁)	156.64	1908.91	2065.55
	(N ₂)	161.36	1837.34	1998.70
	(N ₃)	135.57	1635.61	1771.18
Total Percentage		1213.66	19169.35	15383.01
		7.88	92.12	100.00

TABLE 4
Average crude fat in pounds per acre

Treatments	Crude fat		Total	Intensity of increment
	Grain	Straw		
P_2O_5 levels	(P ₀)	58.82	53.38	112.20
	(P ₁)	64.24	69.62	133.96
Varieties	(V ₁)	56.22	52.26	108.48
	(V ₂)	67.38	73.12	140.50
Nitrogen levels	(N ₀)	53.07	44.93	98.00
	(N ₁)	62.15	63.77	125.92
	(N ₂)	71.76	75.58	147.34
	(N ₃)	61.28	66.18	127.46
Total		495.02	498.84	993.86
Percentage		49.80	50.20	100

TABLE 5
Average mineral matter in pounds per acre

Treatments	Mineral Matter		Total	Intensity of increment
	Grain	Straw		
P_2O_5 level	(P ₀)	107.38	264.38	371.76
	(P ₁)	114.33	306.47	420.80
Varieties	(V ₁)	101.44	245.71	347.15
	(V ₂)	121.51	325.36	446.87
Nitrogen	(N ₀)	95.14	229.94	325.08
	(N ₁)	100.93	286.98	387.91
	(N ₂)	127.84	333.35	461.19
	(N ₃)	110.63	293.37	404.00
Total		879.20	2285.56	3164.76
Percentage		27.78	72.22	100

Table No. 2, Fig. No. 2 show that phosphorus application increased the P_2O_5 uptake of the plant tremendously. The results corroborate the findings of Larson *et al.* (1952) and Beaton and Read (1962). The uptake of P_2O_5 was favoured by nitrogen application due to increased solubility of phosphorus. Similar results were found by Grunes and Kantz (1958), Verma and others (1959) and Miller and Ashton (1960). A greater portion of total uptake of P_2O_5 was found in grain than in straw. Variety 'Green Mountain' was highly responsive to phosphorus application than 'Oat-11'.

Table No. 3 and Fig. 3 reveal that total crude fibre production was positively influenced by phosphorus application but negatively influenced by nitrogen application. Straw was the main part of crude fibre accumulation. Both the varieties differ in their crude fibre production.

Table No. 4 and Fig. 4 show that the application of phosphorus and nitrogen increase the crude fat production of oat crop progressively. This may be due to the fact that phosphorus helps in the interconversion of carbohydrate to fat, whereas nitrogen is responsible for the formation of colouring matter which constitutes the part of the crude fat. Similar results were obtained by Frimmel (1958). The ratio of crude fat in grain and straw was 1 : 1.

Table No. 5 and Fig. 5 show that the amount of mineral matter of oat crop was positively influenced by phosphorus and nitrogen application. It has been reported that phosphorus and nitrogen promote the absorption of other essential macro and micro-elements by crop. The ratio of mineral matter in grain and straw was 2 : 5. Both the varieties 'Green Mountain' and 'Oat-11' differ in their mineral matter contents.

In all the cases, application of 30 lbs. phosphorus per acre showed no significant effect over control. This may be due to the optimum amount of soil phosphorus, originally present in the soil.

The poor results with 90 lbs. nitrogen per acre are due to lodging of the crop, resulting in the low yield of grain and straw.

Acknowledgments

Grateful thanks are due to Dr. A. N. Pathak, Professor and Head of the Department of Agricultural Chemistry, and also to Dr. N. K. Jain, Professor and Head of Agronomy Deptt. for the initiation, keen interest, constant and valuable suggestions.

References

1. Beaton, J. D. and Read, D. W. L. Uptake by oats from a calcareous Saskatchewan soil treated with monoammonium phosphate and its reaction products. *Soil Sci.*, **94** : 404-408, 1962.
2. Berry, R. A. Composition and properties of oat grain and straw. *J. Agri. Sci.*, **10** : 359-414, 1920.
3. Frimmel, G. The importance of fat content in judging Oat crops. *Field crop Abstracts Vol. 12(1)*, 16, 1958.
4. Grunes, D. L. and Kantz, B. A. Nitrogen fertilization increases N, P and K. concentrations in oats. *Agro. J.*, **50** : 729-732, 1958.
5. Larson, W. E., Nelson, L. B. and Hunter, A. S. The effect of phosphate fertilization upon the yield and composition of oats and alfalfa, grown on phosphatic deficient soil. *Agro. J.*, **44** : 357-361, 1952.
6. Miller, M. H. and Ashton, G. C. The influence of fertilizer placement and rate of nitrogen on fertilizer phosphorus utilization by oat. *Canad. J. Soil Sci.*, **40** : 157-167, 1960.
7. Smith, D. Yield and chemical composition of oats for forage with advance in maturity. *Agro. J.*, **52** : 637-638, 1960.
8. Sotola, J. The chemical composition and nutritive value of certain cereal hays as affected by plant maturity. *J. Agri. Research*, **54**, 399, 1937.
9. Stall Cup, O. T. and others. Composition of oat plant as affected by levels of nitrogen fertilization and stage of maturity. *J. Dairy Sci.*, **43**, 867, 1960.
10. Verma, R. D. and others. Studies on the uptake of phosphorus from 32 P labelled superphosphate by crop, Oats. *J. Sc. Fd. Agric.*, **10**(2), 100-107, 1959.

Secondary flow of an Elastico-viscous fluid between two coaxial cones having the same vertex and rotating about a common axis

By

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Abstract

The nature of the secondary flow of a non-Newtonian fluid between two coaxial cones rotating about the common axis with an arbitrary gap angle between the cones is investigated for the following three cases :

- (i) When the inner cone is at rest and outer rotating.
- (ii) When the cones rotate in the same sense, and
- (iii) When the cones rotate in opposite senses.

It is noticed that Newtonian fluids show breaking of the secondary flow only when the cones rotate in the opposite senses for a restricted range of m ($= \frac{\Omega_1}{\Omega_2}$) namely $-3 < m < -1$, Ω_1 and Ω_2 being the angular velocities of inner and outer cones respectively.

A non-Newtonian fluid shows breaking only when $m > 1$ or $m < -1$ and the form of the dividing streamline in these two ranges is found to be quite different for example when $m > 1$, the dividing streamline is circular extending from one cone to the other, while when $m < -1$, it starts from the inner cone and extends to infinity. In the range $-1 \leq m < 1$, Newtonian as well as all non-Newtonian fluids behave the same way and no breaking of the secondary flow is observed.

1. Introduction

The secondary flow of a Rivlin-Ericksen fluid and a Maxwell fluid between two coaxial cones, rotating about an axis passing through the common vertex, with varying angular velocities has been investigated by Bhatnagar and Rathna¹ and by Mohan Rao² respectively. In both of these investigations, the cones are taken to rotate in the same sense. The aim of the present investigation is to study the nature of the secondary flows, in detail, for fluids with varying non-Newtonianity and for arbitrary relative rotation of the two cones with an arbitrary gap angle between them.

In accordance with the theorem recently proved by Bhatnagar³, we include in our present study all the classes of Rivlin-Ericksen⁴, Oldroyd⁵ and Walter's fluids⁶. We note that the equations determining the primary motion and the stream function for the secondary motion are identical for the above mentioned fluids but with the proper interpretation, of the non-Newtonian parameter occurring in it. However, for the Rivlin-Ericksen fluid the stress components differ for the case $(2\phi_2 + \phi_3) \neq 0$, ϕ_2 and ϕ_3 being the coefficients of visco-elasticity and

cross-viscosity respectively. Similar results have been obtained for sphere-sphere geometry by Bhatnagar *et al.*

2. Formulation of the problem

We consider a mass of elasto-viscous fluid confined between two coaxial cones represented by $\theta = \theta_1$ and $\theta = \theta_2$ ($\theta_2 > \theta_1$), in a spherical coordinate system (r, θ, ϕ) with origin at the common vertex of the cones and the polar angle θ and azimuthal angle ϕ being measured from the common axis and some convenient meridian plane respectively. We take the θ_1 cone rotating with an angular velocity Ω_1 and θ_2 cone with an angular velocity Ω_2 such that $\Omega_1 < m \Omega_2$ and m can be positive or negative but real. If u, v, w are the components of velocity in the increasing directions of r, θ, ϕ respectively, the boundary conditions of problem can be written as

$$\left. \begin{aligned} u &= 0, v = 0, w = \Omega_1 r \sin \theta && \text{on } \theta = \theta_1 \\ u &= 0, v = 0, w = \Omega_2 r \sin \theta && \text{on } \theta = \theta_2 \end{aligned} \right\} \quad (2.1)$$

Oldroyd⁵ has given the constitutive equation for a class of elasto-viscous fluids in the form

$$S_{ik} = p_{ik} - \rho g_{ik}, \quad (2.2)$$

$$E_{ik} = \frac{1}{2} (u_{k,i} + u_{i,k}), \quad (2.3)$$

$$p^{ik} + \lambda_1 \frac{\delta p^{ik}}{\delta t} + \mu_0 p_j^j E^{ik} = 2\eta_0 \left(E^{ik} + \lambda_2 \frac{\delta E^{ik}}{\delta t} \right), \quad (2.4)$$

$$\frac{\delta p^{ik}}{\delta t} = \frac{\partial p^{ik}}{\partial t} + u^j p^{ik,j} + \Omega^{i,m} p^{mk} + \Omega^{k,m} p^{im} - E^i_m p^{mk} - E^k_m p^{im}, \quad (2.5)$$

$$\Omega_{ik} = \frac{1}{2} (u_{k,i} - u_{i,k}), \quad (2.6)$$

where S_{ik} is the stress tensor, E_{ik} the rate of strain tensor, Ω_{ik} the vorticity tensor; p_{ik} the part of the stress tensor related to the change of shape of a material element, g_{ik} the metric tensor, ρ an isotropic pressure and u_i the velocity vector, t is the time and a suffix following a comma represents a covariant derivative. η_0 has dimensions of viscosity treated and is taken to be constant and the constant parameters $\lambda_1, \lambda_2, \mu_0$ have dimensions of time.

The constitutive equations for Rivlin-Ericksen and Water's fluids have been recorded in reference^{4,6} respectively.

We now render all the physical and dynamical quantities dimensionless with the help of some length L as the characteristic length and $L \Omega$ as the characteristic velocity where $\Omega = |\Omega_1| + |\Omega_2|$. In such a scheme the hydrostatic pressure will be given by $\eta_0 \Omega p$ and any stress component by $v_0 \Omega p_{ik}$.

The equations of continuity and momentum can then be written in the form

$$g^{ii} u_{i,i} = 0, \quad (2.7)$$

and

$$R \left(\frac{\partial u_i}{\partial t} + u^j u_{i,j} \right) = -p_{,i} + g^{ii} p_{ij}, \quad (2.8)$$

where

$$R = \frac{L^2 \Omega \rho}{\eta_0} \text{ is the Reynolds number.}$$

The boundary conditions in terms of dimensionless variables reduce to

$$\left. \begin{aligned} u = 0, v = 0, \omega = \frac{w}{r \sin \theta} = \frac{\Omega_1}{\Omega} \text{ on } \theta = \theta_1 \\ u = 0, v = 0, \omega = \frac{w}{r \sin \theta} = \frac{\Omega_2}{\Omega} \text{ on } \theta = \theta_2 \end{aligned} \right\} \quad (2.9)$$

3. Perturbation equations and their solutions

Due to the non-linearity of the equation of state and the equations of motion defined in § 2, we treat the Reynolds number R as a small perturbation parameter, so that all the physical and dynamical quantities can be represented as power series in R in the form :

$$\begin{aligned} u &= R g_1(r, \theta) + R^3 g_2(r, \theta) + \dots, \\ v &= R h_1(r, \theta) + R^3 h_2(r, \theta) + \dots, \\ w &= r \sin \theta \omega_0(\theta) + R^2 w_1(r, \theta) + \dots, \\ p_{rr} &= R G_1(r, \theta) + R^3 G_2(r, \theta) + \dots, \\ p_{\theta\theta} &= R K_1(r, \theta) + R^3 K_2(r, \theta) + \dots, \\ p_{\phi\phi} &= R M_1(r, \theta) + R^3 M_2(r, \theta) + \dots, \\ p_{r\theta} &= R L_1(r, \theta) + R^3 L_2(r, \theta) + \dots, \\ p_{\theta\phi} &= F_0(\theta) + R^2 F_1(r, \theta) + \dots, \\ p_{r\phi} &= R^2 H_1(r, \theta) + \dots, \\ p &= R N_1(r, \theta) + R^3 N_2(r, \theta) + \dots. \end{aligned} \quad (3.1)$$

Substituting the above expressions in the equation of state, equations of continuity and momentum and separating various order terms in R , we have the following expressions for the zeroth and first order approximations :

$$F_0 = \sin \theta \frac{d \omega_0}{d \theta}, \quad (3.2)$$

$$O = \frac{1}{r \sin^2 \theta} \frac{d}{d \theta} (\sin^2 \theta F_0), \quad (3.3)$$

$$G_1 = 2 \frac{\partial g_1}{\partial r}, \quad (3.4)$$

$$K_1 = \frac{2}{r} \left(g_1 + \frac{\partial h_1}{\partial \theta} \right), \quad (3.5)$$

$$M_1 = \frac{2}{r} (g_1 + h_1 \cot \theta) + 2 \alpha' \left\{ \sin \theta \frac{d \omega_0}{d \theta} \right\}^2, \quad (3.6)$$

$$L_1 = \frac{1}{r} \frac{\partial g_1}{\partial \theta} + r \frac{\partial}{\partial r} \left(\frac{h_1}{r} \right), \quad (3.7)$$

$$-r \sin^2 \theta \omega_0^2 = -\frac{\partial N_1}{\partial r} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 G_1) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta L_1) - \frac{K_1 + M_1}{r}, \quad (3.8)$$

$$-r \sin \theta \cos \theta \omega_0^2 = -\frac{1}{r} \frac{\partial N_1}{\partial \theta} + \frac{1}{r^3} \frac{\partial}{\partial r} (r^3 L_1) \\ + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta K_1) - \frac{M_1 \cot \theta}{r}, \quad (3.9)$$

$$O = \frac{\partial}{\partial r} (r^2 g_1 \sin \theta) + \frac{\partial}{\partial \theta} (r h_1 \sin \theta), \quad (3.10)$$

where

$$\begin{aligned} a &= a' R = (\lambda_1 - \lambda_2) \Omega \text{ for Oldroyd fluid,} \\ &= \frac{\phi_3 \Omega}{2\eta_0} \text{ for Rivlin-Ericksen fluids subject to the condition that} \\ &= \int_0^\infty \tau N(\tau) d\tau \quad \Omega \text{ for Walter's fluid.} \end{aligned} \quad (3.11)$$

If $2\phi_2 + \phi_3 \neq 0$, then

$$K_1 = \frac{2}{r} \left(g_1 + \frac{\partial h_1}{\partial \theta} \right) + \frac{(2\phi_2 + \phi_3)}{L^2 \rho} \left(\sin \theta \frac{d\omega_0}{d\theta} \right)^2 \quad (3.12)$$

For the sake of simplicity, we call the zeroth order approximation as the primary motion and the first order approximation as the secondary motion.

(a) Primary Motion :

Eliminating F_0 from (3.2) and (3.3) the equation determining the primary motion reduces to

$$\frac{d^2 \omega_0}{d\theta^2} + 3 \cot \theta \frac{d\omega_0}{d\theta} = 0. \quad (3.13)$$

The boundary conditions satisfied by ω_0 are

$$\left. \begin{aligned} \omega_0 &= \frac{\Omega_1}{\Omega} \text{ on } \theta = \theta_1 \\ \omega_0 &= \frac{\Omega_2}{\Omega} \text{ on } \theta = \theta_2 \end{aligned} \right\}. \quad (3.14)$$

Solving (3.13) with the help of boundary conditions (3.14) we have

$$\omega_0 = A_1 [\ln \tan \left(\frac{\theta}{2} \right) - \cot \theta \cosec \theta] + A_2, \quad (3.15)$$

where

$$A_1 = \frac{\Omega_1 - \Omega_2}{\Omega k}, \quad (3.16)$$

$$\begin{aligned} A_2 = \frac{1}{\Omega k} \Big[&\Omega_1 \left\{ \cot \theta_2 \cosec \theta_2 - \ln \tan \left(\frac{\theta_2}{2} \right) \right\} \\ &+ \Omega_2 \left\{ \ln \tan \left(\frac{\theta_1}{2} \right) - \cot \theta_1 \cosec \theta_1 \right\} \Big], \end{aligned} \quad (3.17)$$

and

$$k = \ln \left(\frac{\tan \frac{\theta_1}{2}}{\tan \frac{\theta_2}{2}} \right) + \cot \theta_2 \cosec \theta_2 - \cot \theta_1 \cosec \theta_1. \quad (3.18)$$

(b) Secondary Motion :

The secondary motion is determined with the help of equations (3.4) – (3.10) and the boundary conditions satisfied by g_1 and h_1 are

$$\begin{aligned} g_1 &= h_1 = 0 & \text{on } \theta = \theta_1 \\ g_1 &= h_1 = 0 & \text{on } \theta = \theta_2 \end{aligned} \quad \} \quad (3.19)$$

We now introduce a stream function $\psi(r, \theta)$ given by

$$\begin{aligned} g_1 &= -\frac{1}{r^2 \sin \theta} \frac{\partial \psi}{\partial \theta} \\ h_1 &= \frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r} \end{aligned} \quad \} \quad , \quad (3.20)$$

so that the equation of continuity (3.10) is identically satisfied.

In view of (3.20), the boundary conditions (3.19) take the form

$$\frac{\partial \psi}{\partial \theta} = \frac{\partial \psi}{\partial r} = 0 \text{ on } \theta = \theta_1 \text{ and } \theta = \theta_2. \quad (3.21)$$

Substituting for G_1 , K_1 , M_1 , L_1 from equations (3.4) – (3.7) in equations (3.8), (3.9) and making use of (3.20) the equations determining the secondary motion can be written as

$$\begin{aligned} r \sin^2 \theta \omega_0^2 &= \frac{\partial N_1}{\partial r} + \left(\Delta - \frac{2}{r^2} \right) \left(\frac{1}{r^2 \sin \theta} \frac{\partial \psi}{\partial \theta} \right) - \frac{2}{r^3 \sin \theta} \frac{\partial^2 \psi}{\partial r \partial \theta} \\ &\quad + \frac{2\alpha' \sin^2 \theta}{r} \left(\frac{d \omega_0}{d \theta} \right)^2, \end{aligned} \quad (3.22)$$

and

$$\begin{aligned} -r^2 \sin \theta \cos \theta \omega_0^2 &= -\frac{\partial N_1}{\partial \theta} + r \left[\left(\Delta - \frac{1}{r^2 \sin^2 \theta} \right) \left(\frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r} \right) \right. \\ &\quad \left. - \frac{2}{r^4 \sin \theta} \left(\frac{\partial^2 \psi}{\partial \theta^2} - \cot \theta \frac{\partial \psi}{\partial \theta} \right) \right] - 2\alpha' \sin \theta \cos \theta \left(\frac{d \omega_0}{d \theta} \right)^2, \end{aligned} \quad (3.23)$$

where

$$\Delta \equiv \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{\cot \theta}{r^2} \frac{\partial}{\partial \theta} \quad (3.24)$$

If $(2\phi_2 + \phi_3) \neq 0$ in the case of Rivlin-Ericksen fluids,

$$\alpha' = \frac{1}{\rho L^2} (\phi_2 + \phi_3). \quad (3.25)$$

Eliminating N_1 from the equations (3.22) and (3.23) and putting ψ in the form

$$\psi(r, \theta) = r^5 F_1(\theta) + \alpha' r^3 F_2(\theta), \quad (3.26)$$

the equations determining $F_1(\theta)$ and $F_2(\theta)$ are the following

$$\left(\frac{d^2}{d\theta^2} - \cot \theta \frac{d}{d\theta} + 6 \right) \left(\frac{d^2}{d\theta^2} - \cot \theta \frac{d}{d\theta} + 20 \right) F_1(\theta) \\ = \left[-4A_1 [A_1 \left(\ln \tan \frac{\theta}{2} - \cot \theta \operatorname{cosec} \theta \right) + A_2] \right], \quad (3.27)$$

and

$$\left(\frac{d^2}{d\theta^2} - \cot \theta \frac{d}{d\theta} + 6 \right) \left(\frac{d^2}{d\theta^2} - \cot \theta \frac{d}{d\theta} \right) F_2(\theta) = 32 A_1^2 \cot \theta \operatorname{cosec}^3 \theta, \quad (3.28)$$

which are to be solved with the help of the boundary conditions

$$\left. \begin{aligned} F_1(\theta_1) &= \left(\frac{dF_1}{d\theta} \right)_{\theta=\theta_1} = F_1(\theta_2) = \left(\frac{dF_1}{d\theta} \right)_{\theta=\theta_2} = 0 \\ F_2(\theta_1) &= \left(\frac{dF_2}{d\theta} \right)_{\theta=\theta_1} = F_2(\theta_2) = \left(\frac{dF_2}{d\theta} \right)_{\theta=\theta_2} = 0 \end{aligned} \right\}. \quad (3.29)$$

Since the stream function defined in (3.26) is to the first approximation in R , we define a function

$$\Psi(r, \theta) = R \psi(r, \theta) = r^5 R F_1(\theta) + \alpha r^3 F_2(\theta), \quad (3.30)$$

as the stream function for the secondary motion. $R F_1(\theta)$ represents the contribution of the Newtonian viscosity whereas $\alpha F_2(\theta)$ represents the contribution of the non-Newtonicity of the fluid. Thus as far as the flow properties are concerned all the three types of non-Newtonian fluids behave alike.

It can be easily checked that $F_1(\theta)$ and $F_2(\theta)$ are given by

$$F_1(\theta) = a_1 X_1(\theta) + b_1 X_2(\theta) + c_1 X_3(\theta) + d_1 X_4(\theta) + X_5(\theta) + \frac{A_1 d_2}{39}, \quad (3.31)$$

$$F_2(\theta) = a_2 + b_2 \cos \theta + c_2 X_3(\theta) + d_2 X_4(\theta) + X_5(\theta), \quad (3.32)$$

where

$$X_1(\theta) = 7 \cos^5 \theta - 10 \cos^3 \theta + 3 \cos \theta, \quad (3.33)$$

$$X_2(\theta) = X_1(\theta) \ln \tan \left(\frac{\theta}{2} \right) + 7 \cos^4 \theta + \frac{23}{3} \cos^2 \theta + \frac{16}{15}, \quad (3.34)$$

$$X_3(\theta) = -\cos \theta \sin^2 \theta, \quad (3.35)$$

$$X_4(\theta) = X_3(\theta) \ln \tan \left(\frac{\theta}{2} \right) + \cos^2 \theta - \frac{2}{3}, \quad (3.36)$$

$$\begin{aligned} X_5(\theta) &= A_1^2 \left[\left(\ln \tan \frac{\theta}{2} \right)^2 \left(-\frac{9}{8} \cos^5 \theta + \frac{7}{4} \cos^3 \theta - \frac{5}{8} \cos \theta \right) \right. \\ &\quad \left. + \left(\ln \tan \frac{\theta}{2} \right) \left(-\frac{9}{8} \cos^4 \theta + \frac{11}{4} \cos^2 \theta - \frac{1}{2} \right) - \frac{63}{80} \cos^6 \theta \right. \\ &\quad \left. + \frac{2}{7} \cos^5 \theta + \frac{211}{560} \cos \theta \right], \quad (3.37) \end{aligned}$$

$$X_6(\theta) = -2 A_1^2 \left[\left(\ln \tan \frac{\theta}{2} \right) \cos 2\theta + X_3(\theta) \left(\ln \tan \frac{\theta}{2} \right)^2 + \cos \theta \right], \quad (3.38)$$

and a_1, b_1, c_1, d_1 , and a_2, b_2, c_2, d_2 are to be determined by the boundary conditions (3.29). In the following tables we record the values of the constants for the cases mentioned in the tables :

TABLE I

(θ_1, θ_2)	$m = -3$	$m = -2$	$m = -\frac{1}{2}$	$m = 0$	$m = \frac{1}{2}$	$m = 3$	$m \rightarrow \infty$
$\frac{a_1}{A_1^2}$	(30°, 60°)	-0.262740	-0.266445	-0.281273	-0.296099	-0.340575	-0.229383
	(30°, 90°)	-0.351624	-0.252165	-0.195325	-0.138488	-0.032022	-0.394252
	(86°, 90°)	-0.292877	-0.292838	-0.292679	-0.292522	-0.292046	-0.292333
$\frac{b_1}{A_1^2}$	(30°, 60°)	-0.009054	-0.014477	-0.036183	-0.057886	-0.122994	0.039777
	(30°, 90°)	0.067148	0.002667	-0.034181	-0.071028	-0.181568	0.094783
	(86°, 90°)	0.000528	0.000683	0.001303	0.001923	0.003781	0.000865
$\frac{c_1}{A_1^2}$	(30°, 60°)	0.197757	0.235471	0.386407	0.537324	0.990074	-0.141805
	(30°, 90°)	-0.178086	0.120293	0.290806	0.461322	0.972852	-0.305970
	(86°, 90°)	-0.001846	-0.001727	-0.001252	-0.000777	0.000647	-0.002914
$\frac{d_1}{A_1^2}$	(30°, 60°)	0.065701	0.054562	0.009984	-0.034589	-0.168304	0.165988
	(30°, 90°)	0.047674	0.083949	0.104679	-0.125408	0.187595	0.032127
	(86°, 90°)	0.002595	0.003426	0.006750	0.010076	0.020046	-0.004883

TABLE II

	(30°, 60°)	(30°, 90°)	(86°, 90°)
$\frac{a_2}{A_1^2}$	2.611376	-553456	-0.000047
$\frac{b_2}{A_1^2}$	-6.120945	-3.173563	-1.334249
$\frac{c_2}{A_1^2}$	-6.250740	-7.173563	-5.334249
$\frac{d_2}{A_1^2}$	2.714719	-830184	-0.000071

The stress components up to the first order in R are given by

$$p_{rr} = -2 \operatorname{cosec} \theta \left[3 R r^2 \frac{d F_1}{d \theta} + \alpha \frac{d F_2}{d \theta} \right], \quad (3.49)$$

$$p_{\theta\theta} = 2 R r^2 \operatorname{cosec} \theta \left[4 \frac{d F_1}{d \theta} - 5 F_1 \cot \theta \right] + 2 \alpha \operatorname{cosec} \theta \left[2 \frac{d F_2}{d \theta} - 3 F_2 \cot \theta \right], \quad (3.40)$$

$$p_{\phi\phi} = 2 R r^2 \operatorname{cosec} \theta \left[5 F_1 \cot \theta - \frac{d F_1}{d \theta} \right] + 2 \alpha \operatorname{cosec} \theta \left[4 A_1^2 \operatorname{cosec}^3 \theta + 3 F_2 \cot \theta - \frac{d F_2}{d \theta} \right], \quad (3.41)$$

$$p_{r\theta} = R r^2 \operatorname{cosec} \theta \left[-\frac{d^2 F_1}{d \theta^2} + \cot \theta \frac{d F_1}{d \theta} + 10 F_1 \right] + \alpha \operatorname{cosec} \theta \left[-\frac{d^2 F_2}{d \theta^2} + \cot \theta \frac{d F_2}{d \theta} \right], \quad (3.42)$$

$$p_{\theta\phi} = 2 A_1 \operatorname{cosec}^2 \theta, p_{r\phi} = 0 \quad (3.43)$$

When $(2 \phi_2 + \phi_3) \neq 0$ for Rivlin-Ericksen fluids then the stress component $p_{\theta\theta}$ changes and is given by

$$p_{\theta\theta} = 2 R r^2 \operatorname{cosec} \theta \left[4 \frac{d F_1}{d \theta} - 5 F_1 \cot \theta \right] + 2 \alpha \operatorname{cosec} \theta \left[2 \frac{d F_2}{d \theta} - 3 F_2 \cot \theta \right] + \frac{(2 \phi_2 + \phi_3)}{\eta_0} (4 A_1^2 \operatorname{cosec}^4 \theta). \quad (3.44)$$

From the above expressions for the secondary stresses it is clear that when $(2\phi_2 + \phi_3) = 0$ all the three types of fluids have the same stresses and that only the stress $\rho_{\theta\theta}$ for the Rivlin-Ericksen fluids with $(2\phi_2 + \phi_3) \neq 0$ differs from that for the other two types of fluids but by a quantity proportional to $(2\phi_2 + \phi_3)$.

4. Discussion of the results

In the primary motion the streamlines in any plane perpendicular to the axis of the cones are concentric circles having centres on this axis.

We shall now discuss in detail the behaviour of the secondary flow, which is induced in the meridian plane for various values of m . For our numerical work we have taken the following gap angle between the cones 4° , 30° and 60° .

We shall, however, discuss here the secondary flow only when the gap angle is 30° as the nature of the flow remains the same in other cases also.

Case (i) : Let $m = 0$. When the inner cone ($\theta_1 = 30^\circ$) is at rest and the outer cone ($\theta_2 = 60^\circ$) is rotating we note that the entire flow field for Newtonian as well as for all non-Newtonian (e.g. $\alpha' = 0.02, 0.04$ etc.) fluids consists of only one type of streamlines. The fluid is drawn in at the cone which is held at rest almost parallel to it and is thrown out at the cone which is rotating. Whatever be the magnitude of the rotation of the outer cone, neither Newtonian nor non-Newtonian fluids show any breaking. Fig. 1 depicts the streamlines $\psi = 0.002$ and $\psi = 0.2$ for a non-Newtonian fluid $\alpha' = 0.02$.

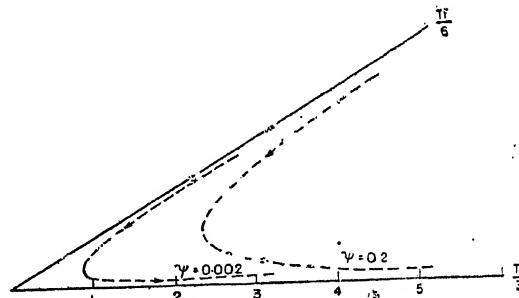


FIG. 1 THE STREAM LINES FOR A NON-NEWTONIAN FLUID WHEN THE INNER CONE IS AT REST AND OUTER ROTATING ($m = 0, \alpha' = 0.02$).

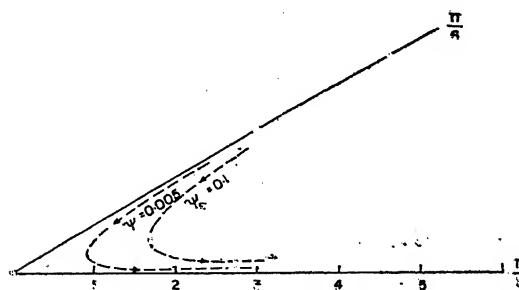


FIG. 2 THE STREAM LINES FOR A NON-NEWTONIAN FLUID WHEN THE CONES ROTATE IN THE SAME SENSE ($m = 1/2, \alpha' = 0.02$).

Case (ii) : Let $m > 0$, i.e. both the cones rotate in the same sense.

(a) Let $0 < m < 1$ so that the inner cone rotates with a smaller angular velocity than the outer cone. We note that here also the entire flow field for Newtonian as well as for all non-Newtonian fluids (e.g. $\alpha' = 0.02, 0.04$ etc.) consists of only one type of streamlines, the direction of flow being the same as in case (i). Thus there is no breaking of the secondary flow. Fig. 2 depicts the streamlines $\psi = 0.005$ and $\psi = 0.1$ for a non-Newtonian fluid with $\alpha' = 0.02$ and $m = \frac{1}{2}$.

(b) Let $m \geq 1$. When $m = 1$, i.e. the cones rotate with the same angular velocity and in the same sense, there is no secondary flow and only the primary motion exists for all values of α' . In fact the entire system rotates as a rigid body.

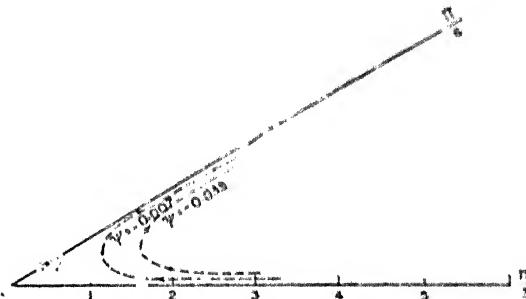


FIG. 3 THE STREAM LINES FOR A NEWTONIAN FLUID WHEN THE CONES ROTATE IN THE SAME SENSE. ($m=3$, $\alpha=0$)

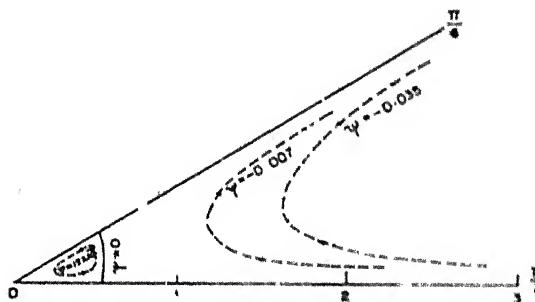


FIG. 4 THE STREAM LINES FOR A NON-NEWTONIAN FLUID WHEN THE CONES ROTATE IN THE SAME SENSES ($m=3$, $\alpha=0.041$)

As m increases from unity, i.e. the inner cone rotates with a greater angular velocity than the outer, the secondary flow appears again. We notice that for a Newtonian fluid the direction of the streamlines is opposite to those which existed for values of $0 < m < 1$, i.e., the fluid is drawn in at the outer cone and thrown away near the inner cone. Fig. 3 depicts the streamlines $\psi = -0.007$ and $\psi = -0.035$ showing such a behaviour for $m = 3$.

When $m > 1$, $F_1(\theta)$ is always negative definite and $F_2(\theta)$ is always positive definite for all values of θ between 30° and 60° . This fact exhibits that even for

very small values of α' , whatever m may be, the flow field breaks into two distinct regions, the dividing streamline $\psi = 0$ being given by

$$r = \left[\frac{a F_2(\theta)}{-R F_1(\theta)} \right]^{\frac{1}{2}} = r_0.$$

This dividing streamline extends from one cone to the other and is almost circular. In the region nearer to the vertex, the streamlines form closed loops and in the outer region the fluid flows more or less parallel to the generators of the cone to which it is closest, being drawn in at the outer cone and thrown out at the inner. For a fixed value of m , as α' increases the dividing stream line moves away from the vertex, Fig. 4 depicts such a breaking of the secondary flow for non-Newtonian fluid with $\alpha' = 0.04$ and $m = 3$. The above mentioned behaviour of secondary flow for Newtonian and non-Newtonian fluids prevails even when m becomes very large and finally tends to infinity. In Fig. 5 we have drawn the streamlines for $m \rightarrow \infty$ and non-Newtonian fluid characterised by $\alpha' = 0.04$ depicting the breaking of the secondary flow.

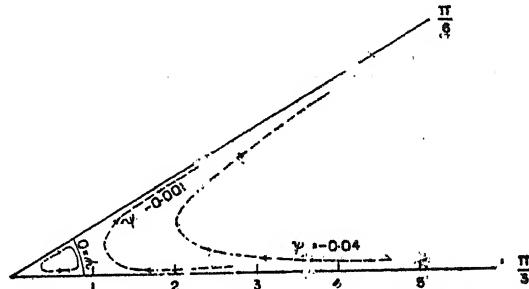


FIG. 5 THE STREAM LINES FOR A NON-NEWTONIAN FLUID WHEN THE OUTER CONE IS AT REST ($m=\infty, \alpha'=0.04$)

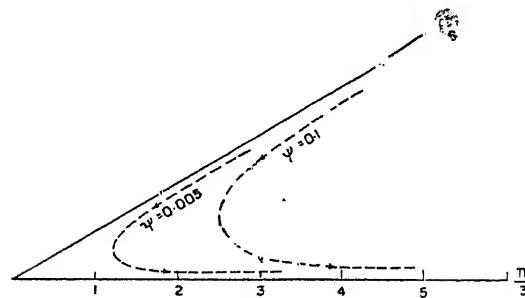


FIG. 6 THE STREAM LINES FOR A NON-NEWTONIAN FLUID WHEN THE CONES ROTATE IN OPPOSITE SENSES ($m=-1/2, \alpha'=0.02$)

Case (iii) : Let $m < 0$, i.e. the two cones rotate in opposite senses. We consider the following two ranges for m : (a) $0 > m \geq -1$ and (b) $m < -1$.

Case (a) : $0 > m \geq -1$, i.e. when the inner cone rotates in the opposite sense with a smaller angular velocity than that of the outer cone, the secondary flow for Newtonian as well as for all non-Newtonian fluids resembles the one for $0 < m < 1$. There is no breaking of the secondary flow. Fig. 6 depicts the stream lines $\psi = 0.005$ and $\psi = 0.1$ for $m = -\frac{1}{2}$ and for a non-Newtonian fluid with $\alpha' = 0.02$.

(b) Let $m < -1$. When $-1 > m > -3$, we notice that both the Newtonian and the non-Newtonian fluids show breaking of the secondary flow.

For Newtonian fluids, this breaking is purely due to the motion of the two cones. The region between the cones is divided into two distinct regions by a streamline $\psi = 0$ given by $\theta \approx \theta_c$ passing through the common vertex of the cones and extending to infinity. The direction of flow in these regions is opposite to each other although the streamlines are similar. In the region $\frac{\pi}{6} < \theta < \theta_c$ the fluid is drawn in at $\theta = \theta_c$ almost parallel to it and thrown out at the inner cone, while in the region $\theta_c < \theta < \frac{\pi}{3}$ it is thrown out at the outer cone. Fig. 7 shows such a breaking of secondary flow of a Newtonian fluid for $m = -2$. We note that here $\theta_c \approx 45^\circ$. As m decreases further, the streamline $\psi = 0$ goes on shifting towards the outer cone and for some critical m_c of m , $m_c \approx 3$, the entire flow field is filled up with only one type of streamlines, the direction of flow now being opposite to that which existed prior to the breaking, i.e. the fluid is drawn in at the outer cone and thrown out at the inner. In Fig. 8 we have drawn typical streamlines

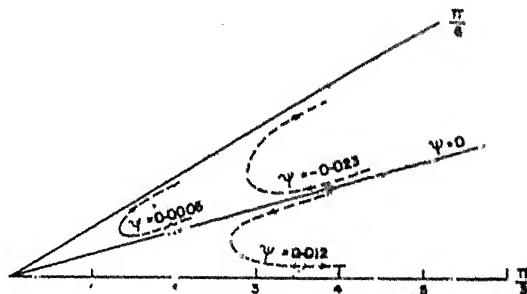


FIG. 7 THE STREAM LINES FOR A NEWTONIAN FLUID WHEN THE CONES ROTATE IN THE OPPOSITE SENSES ($m = -2, \alpha' = 0$)

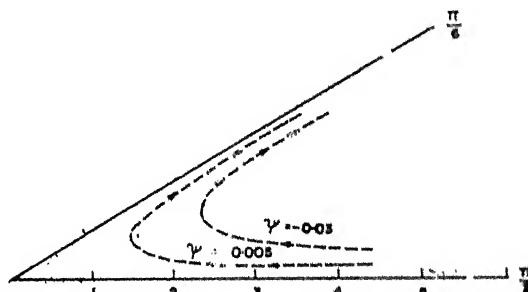


FIG. 8 THE STREAM LINES FOR A NEWTONIAN FLUID WHEN THE CONES ROTATE IN THE OPPOSITE SENSES ($m = -3, \alpha' = 0$)

$\psi = -0.005$ and $\psi = -0.03$ to depict such a behaviour of Newtonian fluid for the case $m = -3$. Once such a reversal of the flow field takes place, it will maintain this character as m decreases further.

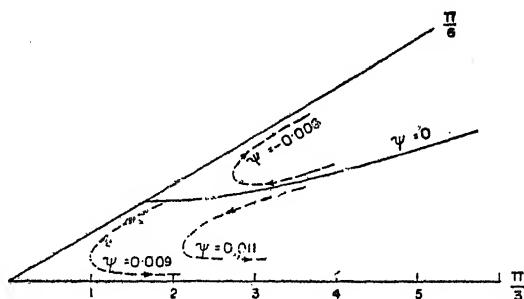


FIG. 9 THE STREAM LINES FOR A NON-NEWTONIAN FLUID WHEN THE CONES ROTATE IN OPPOSITE SENSES ($m = -2, \alpha' = 0.04$)

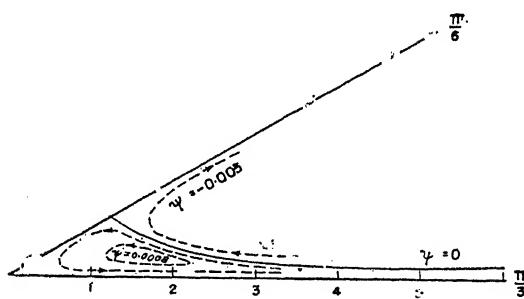


FIG. 10 THE STREAM LINES FOR A NON-NEWTONIAN FLUID WHEN THE CONES ROTATE IN OPPOSITE SENSES ($m = -3, \alpha' = 0.04$)

For a non-Newtonian fluid, the secondary flow breaks even for very small values of α' and for a fixed m . The streamline $\psi = 0$ divides the entire region into two distinct regions, the direction of flow in one being opposite to that of the other. The dividing streamline always starts on the inner cone and extends to infinity almost parallel to the outer cone at large distances from the common vertex. In Fig. 9 we have drawn the streamlines for a non-Newtonian fluid $\alpha' = 0.04$ for $m = -2$. We note that the dividing streamline $\psi = 0$ meets the inner cone at a distance $r \approx 2.0$ and extends to infinity. In the region lying between the inner cone and the dividing streamline, the fluid is drawn in at the dividing streamline and thrown out at the inner cone almost parallel to it; in the region between the dividing streamline and the outer cone the fluid is thrown out near the outer cone. We do not, however, observe the streamline in the form of closed loops in this case. For a fixed m , as α' increases the point where the streamline $\psi = 0$ meets the inner cone shifts away from the vertex. For a fixed α' as m decreases, for example for $m = -3$. (Fig. 10), the dividing streamline $\psi = 0$ shifts towards the outer cone and the point where it meets the inner cone shifts towards the vertex thus reducing the region between $\psi = 0$ and the outer cone. In the

region between $\psi = 0$ and the inner cone the fluid is thrown out at the inner cone while it is drawn in parallel to the dividing stream line. In the region between $\psi = 0$ and the outer cone the streamlines seem to form elongated closed loops as indicated by the streamline $\psi = 0.0008$.

We sum up our conclusions as follows :

(i) The secondary flow of Newtonian fluids only shows breaking when the cones rotate in opposite senses for a restricted range of m , namely $-3 < m_c < m < -1$. The breaking of the flow for these fluids is purely due to the motion of the boundaries.

(ii) The secondary flow of non-Newtonian fluids shows breaking only when $m > 1$ or $m < -1$. The form of the dividing streamline $\psi = 0$ is quite different for these two ranges of m : when $m > 1$, the dividing streamline is circular extending from one cone to the other, while when $m < -1$ the dividing streamline starts from the inner cone and extends to infinity. For a fixed m ($m > 1$ or $m < -1$) all non-Newtonian fluids show breaking of the secondary flow. As the non-Newtonian parameter increases, the dividing streamline shifts away from the vertex.

(iii) In the range $-1 \leq m < 1$, Newtonian as well as all non-Newtonian fluids behave in the same way.

(iv) When $2\phi_2 + \phi_3$ is zero for a Rivlin-Ericksen fluid, all the three types of non-Newtonian fluids behave identically for the same value of a . Even when $2\phi_2 + \phi_3 \neq 0$ all the types of fluids have identical flows and stresses except the $\rho_{\theta\theta}$ component for the Rivlin-Ericksen fluid which differs from $\rho_{\theta\theta}$ for the other two types of fluids by a term which is proportional to $2\phi_2 + \phi_3$.

References

1. Bhatnagar, P. L. and Rathna, S. L. *Quart. Jour. Mech. App. Math.*, **XVI**, 329, 1963.
2. Rao, D. K. M. *Proc. Ind. Acad. Sci.*, **LVI**, 198, 1962.
3. Bhatnagar, P. L. (To be published).
4. Rivlin, R. S. and Ericksen, J. L. *Jour. Rat. Mech. and Analy.*, **4**, 329, 1955.
5. Oldroyd, J. G. *Proc. Roy. Soc.*, **200A**, 523, 1950.
6. Walters, K. *Quart. Jour. Mech. App. Math.*, **15**, 76, 1962.
7. Bhatnagar, P. L., Rajagopalan Renuka and Mathur, M. N. Communicated to Indian Journal of Mathematics.